PB85-241529

Atmospheric Fates of Organic Chemicals Prediction of Ozone and Hydroxyl Radical Reaction Rates and Mechanisms

California Univ., Riverside

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Aug 85

U.S. Department of Commerce
National Technical Information Service
NTIS.

PB85-241529

EPA/600/3-85/063
August 1985

ATMOSPHERIC FATES OF ORGANIC CHEMICALS: Prediction of Ozone and Hydroxyl Radical Reaction Rates and Mechanisms

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Cooperative Agreement Number CR-809247

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U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

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SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/3-85/063	2.
3. RECIPIENT'S ACCESSION NO. PB85 241529	
4. TITLE AND SUBTITLE ATMOSPHERIC FATES OF ORGANIC CHEMICALS: Prediction of Ozone and Hydroxyl Radical Reaction Rates and Mechanisms	5. REPORT DATE August 1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R. Atkinson, W. P. L. Carter, S. M. Aschmann, J. N. Pitts, Jr., A. M. Winer	8. PERFORMING ORGANIZATION REPORT NO
9. PERFORMING ORGANIZATION NAME AND ADDRESS Statewide Air Pollution Research Center University of California Riverside, California 92521	10. PROGRAM ELEMENT NO. CCUL1A/02-1138 (FY-85)
	11. CONTRACT/GRANT NO. Cooperative Agreement 809247
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Sciences Research Laboratory-RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED Final 2/82 - 2/85
	14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 86
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

The information in this document has been funded by the United States Environmental Protection Agency under Cooperative Agreement number CR-809247 to Statewide Air Pollution Research Center, University of California, Riverside, California. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commerical products does not constitute endorsement or recommendation for use.

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1. INTRODUCTION

Thousands of industrial chemicals, many of which are critical to our economy, are in use today. Recently, however, there has been growing recognition of the need to understand the environmental fates of these chemicals, including their distribution, potential by-products, toxicity and ecological effects, as well as their environmental sinks and lifetimes. Unfortunately, these factors are often poorly characterized or, in many cases, completely undetermined. In order to provide such data, which are essential for risk assessments for existing and new chemicals, the national Toxic Substance Control Act (TSCA) was passed by Congress and became effective January 1, 1977. The provisions of the Act deal with four principal areas: information gathering, regulation, premanufacture screening and interagency cooperation.

One major goal of TSCA is to develop a sufficiently large data base concerning the environmental fates of chemicals so that accurate a-priori predictions can be made concerning newly developed chemicals, or for chemicals presently in use for which little or no experimental data exist. Ready access to such an extensive and reliable data base would then permit a cost-effective and rapid assessment of the environmental impact of both existing and newly developed chemicals.

During the past decade, the general features of the gas phase chemistry occurring in polluted urban atmospheres, and indeed in the natural troposphere, have been extensively investigated, and at least a semiquantitative understanding now exists for the simpler NO_x-organic-air photooxidation systems (Hendry et al. 1978, 1980, Carter et al. 1979, Whitten et al. 1979, 1980, Atkinson et al. 1980, Atkinson and Lloyd 1984). From these data, obtained from both laboratory and smog chamber studies, it is now recognized that under ambient atmospheric conditions in both the polluted and natural troposphere the homogeneous gas phase loss processes of organics are essentially totally due to photodissociation, reaction with ozone (O_3) or reaction with hydroxyl (OH) and nitrate (NO_3) radicals (Atkinson et al. 1979, Herron et al. 1979, Hendry and Kenley 1979, Atkinson and Lloyd 1984, Atkinson and Carter 1984, Atkinson 1985).

Thus, in order to ascertain the fates of organic compounds emitted into the lower atmosphere, it is first of all necessary to know their

rates of reaction with O_3 and with OH radicals (and, for certain classes of organics, NO_3 radicals) together with their photolysis rates. Having determined the primary loss process(es) under atmospheric conditions, it is then necessary to ascertain the mechanism and products of this loss process.

Under the Toxic Substances Control Act there are many hundreds if not thousands of compounds which ultimately will need to be screened and investigated with regard to their atmospheric fate. Clearly, a "blanket," full scale experimental approach of investigating every chemical, while technically feasible, is neither cost- nor time-effective. Thus, it is evident that there is a need to be able to accurately predict the rate constants for O_3 and OH radical reactions, and to predict photolysis rates. The latter appears to be inherently more difficult (Hendry and Kenley 1979), but, with a knowledge of the absorption cross-section, upper limits to the photodissociation rates may be calculated readily (Pitts et al. 1981a). The use of such a-priori estimation procedures then allows a rapid and cost-effective pre-screening of organics to determine their major loss processes under atmospheric conditions.

Following the use of such pre-screening predictive techniques, further experimental work may be necessary to obtain more quantitative data on one or more of the possible loss processes. This will depend upon the absolute and relative magnitudes of the estimated OH and NO_3 radical and O_3 reaction rates as well as the estimated maximum photolysis rate under atmospheric conditions. Once the major atmospheric sink(s) and its rate(s) is (are) known, then the reaction or photodissociation pathways can be estimated, provided that an extensive and critically evaluated data base concerning OH and NO_3 radical and O_3 reaction mechanisms, and photodissociation pathways, is readily available. A schematic approach to the evaluation of atmospheric loss processes and their products is shown in Figure 1.

The Atmospheric Sciences Research Laboratory of the U. S. Environmental Protection Agency (EPA) contracted, via this cooperative agreement, the Statewide Air Pollution Research Center (SAPRC), University of California, Riverside, to establish a critically-evaluated data base for the rate constants and atmospheric reaction mechanisms of the reactions of O_3 and OH radicals with organics. Furthermore, this cooperative agreement

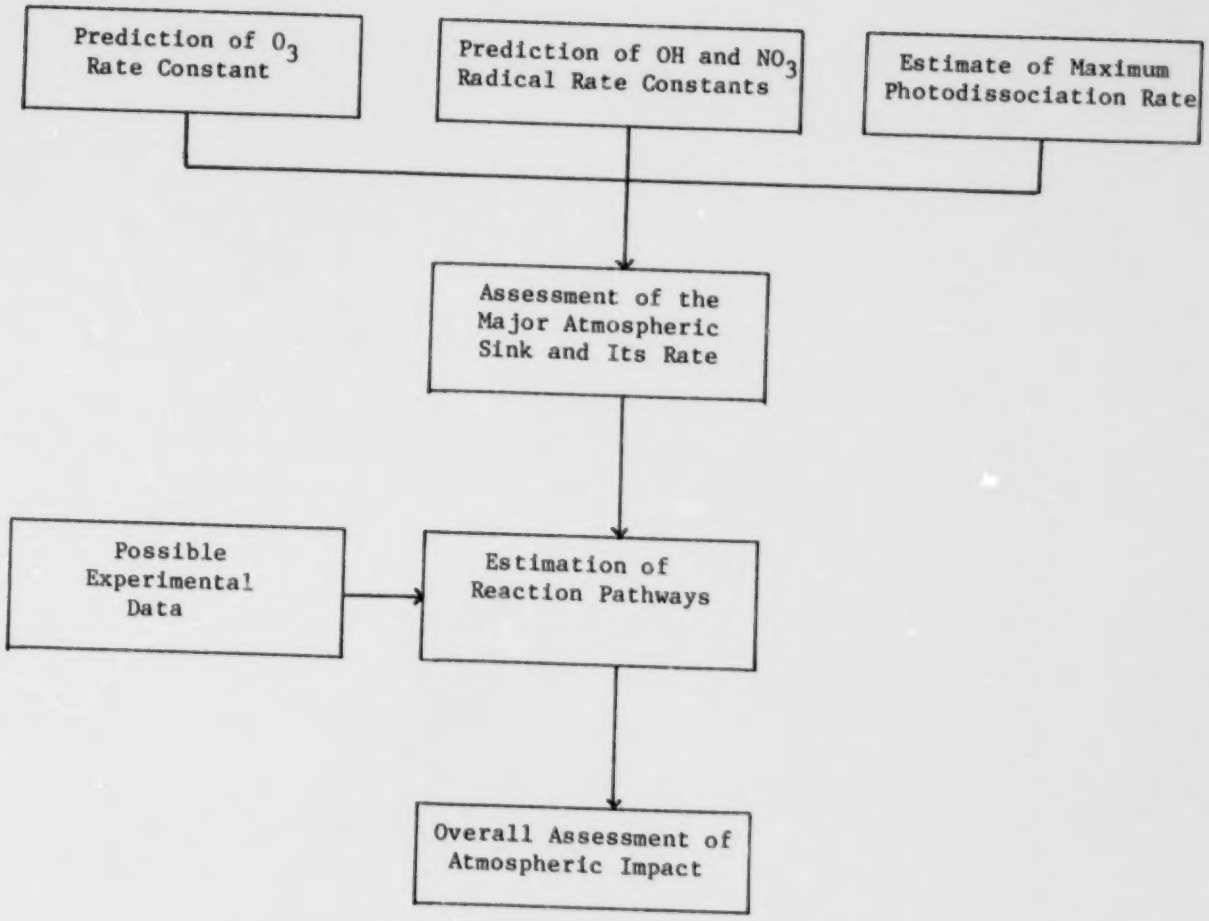

Prediction of O_3 Rate Constant
Prediction of OH and NO_3 Radical Rate Constants
Estimate of Maximum Photodissociation Rate
Assessment of the Major Atmospheric Sink and Its Rate
Possible Experimental Data
Estimation of Reaction Pathways
Overall Assessment of Atmospheric Impact

Figure 1. Schematic approach using predictive capabilities to assess the atmospheric impact of emitted organics.

called for the development of predictive relationships for the estimation of O_3 and OH radical rate constants for organics for which no experimental data are available.

In the following sections, the specific objectives of this program, a summary of the experimental research carried out, and a discussion dealing with a-priori predictive techniques for O_3 and OH radical reaction rate constants are given.

2. OBJECTIVES

The overall objectives of this three-year program were:

1. To critically evaluate the literature and develop a data base for the rate constants for the gas phase reactions of O_3 and the OH radical with organics.

2. To investigate, using this data base, predictive relationships based on the molecular structures of organics with the goal of developing accurate means of predicting O_3 and OH radical rate constants for compounds for which experimental data are not available.

3. To critically evaluate, concurrently with these objectives, the literature dealing with the mechanistic aspects of these O_3 and OH radical reactions with organics under atmospheric conditions.

4. Since it was readily apparent that significant gaps in our knowledge of rate constants for the reactions of O_3 and of OH radicals with organic compounds existed, a modest, but highly focussed, experimental program was carried out to determine O_3 and/or OH radical reaction rate constants for selected organics for which experimental data were not available. The organic compounds studied included, at the request of the EPA, the three monochlorobiphenyl isomers. These experimental studies were carried out using the protocols previously developed and tested at SAPRC for the EPA (Pitts et al. 1981b, 1982).

3. EXPERIMENTAL PROGRAM

As noted above, the experimental techniques employed were essentially identical to the experimental protocols previously developed and tested at SAPRC (Pitts et al. 1981b, 1982).

Experimental Determination of Rate Constants for Reaction of O_3 with Organics

Ozone reaction rate constants were determined at room temperature using the experimental technique described in detail by Pitts et al. (1981b). This technique is based upon monitoring the increased rates of O_3 decay in the presence of known concentrations of a reactive organic. Under these conditions, the reactions removing O_3 are:

$$O_3 + \text{wall} \rightarrow \text{loss of } O_3 \qquad (1)$$

$$O_3 + \text{reactant} \rightarrow \text{products} \qquad (2)$$

and, hence,

$$-d[O_3]/dt = (k_1 + k_2[\text{reactant}])[O_3] \qquad (I)$$

Under the experimental conditions employed, the reactant concentrations are greatly in excess of the initial O_3 concentrations (i.e., $[\text{reactant}]/[O_3]_{\text{initial}} \geq 10$). Hence, equation (I) may be rearranged to yield

$$-d\ln[O_3]/dt = k_1 + k_2[\text{reactant}] \qquad (II)$$

and, from the ozone decay rates, $-d\ln[O_3]/dt$, at various reactant concentrations, and with a knowledge of the background O_3 decay rate, k_1, the rate constants k_2 may be obtained.

The majority of the experiments were carried out in ~175 liter FEP Teflon reaction bags which were initially divided into two subchambers by metal barriers. Ozone, at concentrations so as to obtain ~1 ppm in the entire reaction bag, was injected in pure air diluent into one subchamber. A known amount of the organic in pure air diluent was injected into the other subchamber. The reactions were initiated by removing the barriers and rapidly mixing the contents of the reaction bag by pushing

down on alternative sides of the bag for ~1 minute. Ozone concentrations were, after mixing of the reactants, monitored as a function of time by a chemiluminescence analyzer and in certain cases the organic concentrations in the entire bag were quantitatively analyzed by gas chromatography with flame ionization detection. This technique can be used for the determination of O_3 reaction rate constants $\lesssim 5 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}, which encompasses the vast majority of organics encountered to date.

For naphthalene, biphenyl and the three monochlorobiphenyl isomers, upper limits to the rate constants k_2 were derived from the lack of any observable organic decay rate in the presence of excess O_3, in a ~6400 liter all-Teflon environmental chamber (Atkinson et al. 1984a, Atkinson and Aschmann 1985).

Determination of Rate Constants for the Reaction of OH Radicals with Organics

Hydroxyl radical reaction rate constants were determined at room temperature using the relative rate technique developed and extensively tested at SAPRC (Atkinson et al. 1982a, Pitts et al. 1982). Hydroxyl radicals were generated by the photolysis, at wavelengths $\gtrsim 290$ nm, of methyl nitrite (CH_3ONO) in air at part-per-million concentrations:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

In order to minimize the formation of O_3 during these irradiations, NO was added to the reaction mixtures, which had typical initial concentrations of: CH_3ONO, ~5-15 ppm; NO, ~5 ppm and ~1 ppm each of the reference organic and the reactant. Ultrazero air (<0.1 ppm hydrocarbons) was used as the diluent gas.

Irradiations were carried out in a ~60-liter cylindrical FEP Teflon reaction bag, surrounded by 24 15-Watt blacklights, or in a ~6400-liter all-Teflon environmental chamber, also equipped with blacklight irradiation (Figure 2). The organic reactants were quantitatively monitored by

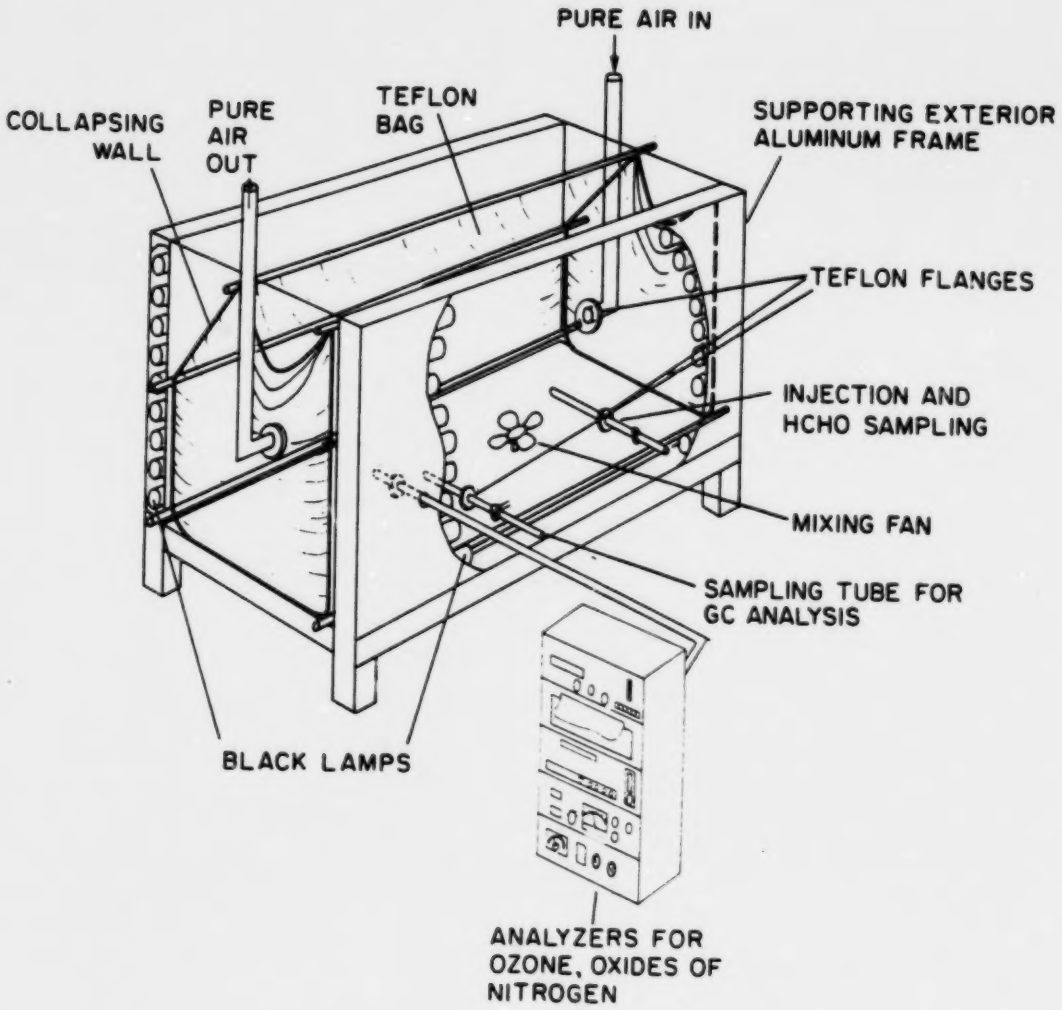


Figure 2. 6400-liter all-Teflon chamber.

gas chromatography with flame ionization detection prior to and during the irradiations.

In these reaction mixtures, the OH radicals react with both the reference organic and the reactant organic:

$$\text{OH} + \text{reactant} \rightarrow \text{products} \qquad (3)$$

$$\text{OH} + \text{reference organic} \rightarrow \text{products} \qquad (4)$$

For organics which do not photolyze or react to any significant extent with other reactive species, the following expression can be derived (Atkinson et al. 1982a):

$$\ln\left(\frac{[\text{reactant}]_{t_o}}{[\text{reactant}]_t}\right) = \frac{k_3}{k_4} \ln\left(\frac{[\text{reference organic}]_{t_o}}{[\text{reference organic}]_t}\right) \qquad \text{(III)}$$

where $[\text{reactant}]_{t_o}$, $[\text{reference organic}]_{t_o}$ are the concentrations of the reactant and the reference organic, respectively; at time t_o, $[\text{reactant}]_t$, $[\text{reference organic}]_t$ are the corresponding concentrations at time t; and k_3 and k_4 are the rate constants for reactions (3) and (4), respectively. Hence, plots of $\ln([\text{reactant}]_{t_o}/[\text{reactant}]_t)$ against $\ln([\text{reference organic}]_{t_o}/[\text{reference organic}]_t)$ have a slope of k_3/k_4 and zero intercept.

For organics which can also photolyze, a more complex expression is derived,

$$\frac{1}{(t-t_o)} \ln\left(\frac{[\text{reactant}]_{t_o}}{[\text{reactant}]_t}\right) = k_5 + \frac{k_3}{k_4(t-t_o)} \ln\left(\frac{[\text{reference organic}]_{t_o}}{[\text{reference organic}]_t}\right) \qquad \text{(IV)}$$

where k_5 is the rate constant for the photolysis reaction:

$$\text{reactant} + h\nu \rightarrow \text{products} \qquad (5)$$

In this case, a plot of the left hand side of this equation against $(t-t_o)^{-1}$ ln([reference organic]$_{t_o}$/[reference organic]$_t$) yields a straight line of slope k_3/k_4 and intercept k_5. Knowing the rate constant k_4 for the reference organic, k_3 may be derived in either case.

Results of Experimental Program

The experimental studies carried out are described in detail in the publications of Atkinson et al. (1983a-d, 1984a-c) and Atkinson and Aschmann (1984a-c, 1985). These individual studies and the results obtained are briefly summarized below [for the OH radical reaction rate constants, the rate constant ratios k_3/k_4 have been placed on an absolute basis using the values of k_4 for the reference organics as recommended by Atkinson (1985)].

- In order to investigate the effects of ring strain on abstraction rate constants, the rate constants for the reactions of OH radicals with a series of bi- and tri-cyclic alkanes at 299 ± 2 K were determined. The data show, as discussed in detail by Atkinson et al. (1983a), that for overall ring strain energies of >5 kcal mole^{-1} the rate constants are lowered over those predicted for the strain-free molecules by significant amounts. The kinetic data obtained are given in Table 1.

- The rate constants for the reactions of O_3 and OH radicals with furan and thiophene were measured at 298 ± 2 K. The OH radical rate constants for these two five-membered heterocyclics were found to be significantly lower than would be anticipated by analogy with other dialkenes. Although further work is necessary for other members of these homologous series, these data indicate that the resonance stabilization in these organics (~22 kcal mole^{-1} for thiophene and ~12 kcal mole^{-1} for furan) is responsible for the decreased rate constants. The data obtained are given in Table 2, and the results are discussed in detail by Atkinson et al. (1983b).

- In order to study the effect of ring strain on O_3 addition rate constants, the rate constants for the reaction of O_3 with a series of cycloalkenes were measured at 298 ± 2 K. It was found that a reasonable correlation exists between the rate constants per >C=C< double bond and the strain energy released when the double bond which reacts with O_3 is replaced by a single bond. The rate constants obtained are given in Table 3, and are discussed in detail by Atkinson et al. (1983c).

Table 1. Rate Constants k for the Gas Phase Reaction of OH Radicals with a Series of Bi- and Tri-Cyclic Alkanes at 299 ± 2 K

Alkane	Strain Energy (kcal mole^{-1})	10^{12} x k (cm^3 molecule^{-1} s^{-1})[a]
Bicyclo[2.2.1]heptane	16.1	5.42 ± 0.14
Bicyclo[2.2.2]octane	9.6	14.5 ± 1.0
Bicyclo[3.3.0]octane	11.1	10.9 ± 0.6
cis-Bicyclo[4.3.0]nonane	7.9	17.0 ± 1.2
trans-Bicyclo[4.3.0]nonane	6.9	17.4 ± 1.3
cis-Bicyclo[4.4.0]decane	2.9	19.6 ± 1.4
trans-Bicyclo[4.4.0]decane	-0.3	20.2 ± 1.2
Tricyclo[5.2.1.$0^{2,6}$]decane	22.8	11.2 ± 0.4
Tricyclo[3.3.1.$1^{3,7}$]decane	4.2-6.6	22.7 ± 2.0

[a]The error limits are two standard deviations.

Table 2. Rate Constants for the Reactions of Ozone and Hydroxyl Radicals with Furan and Thiophene at 298 ± 2 K[a]

	10^{18} x k^{O_3} (cm^3 molecule^{-1} s^{-1})	10^{12} x k^{OH} (cm^3 molecule^{-1} s^{-1})
Furan	2.42 ± 0.28	39.3 ± 2.8
Thiophene	<0.06	9.37 ± 0.34

[a]The error limits are two standard deviations.

Table 3. Rate Constants k for the Reaction of O_3 with a Series of Cycloalkenes

Cycloalkene	10^{16} x k (cm^3 molecule^{-1} s^{-1})[a]
Cyclopentene	2.75 ± 0.33
Cyclohexene	1.04 ± 0.14
Cycloheptene	3.19 ± 0.36
1,3-Cyclohexadiene	19.7 ± 2.8
1,4-Cyclohexadiene	0.639 ± 0.074
Bicyclo[2.2.1]-2-heptene	21.4 ± 3.5
Bicyclo[2.2.1]-2,5-heptadiene	46.8 ± 12.9
Bicyclo[2.2.2]-2-octene	0.728 ± 0.090

[a]Indicated error limits are two least squares standard deviation.

• The rate constants for the reactions of OH radicals with a series of cycloalkenes were determined at room temperature in order to investigate the effect of ring strain on these rate constants. The rate constants obtained are given in Table 4, and, in contrast to the O_3 reactions, no effect of ring strain was observed. From these data, a predictive technique for the estimation of OH radical rate constants for alkenes, cycloalkenes and conjugated acyclic and cyclic dialkenes was derived, as described in detail by Atkinson et al. (1983d).

• Rate constants for the reaction of O_3 and OH radicals with acetylene, propyne and 1-butyne were determined at room temperature, since earlier unpublished data from this laboratory had indicated that the rate constant for the reaction of O_3 was a factor of ~4 lower than the reported literature values. The kinetic data obtained are given in Table 5, and are discussed in detail by Atkinson and Aschmann (1984a).

• In order to derive predictive relationships for the reaction of OH radicals with branched alkanes, rate constants were determined for a series of these alkanes (Table 6). These data, when combined with those obtained previously in these laboratories for a series of n-alkanes (Atkinson et al. 1982b) allowed an a priori predictive technique to be derived for the estimation of OH radical rate constants for alkanes, including strained cycloalkanes. This a-priori predictive approach is discussed in detail by Atkinson et al. (1984b) and in the sections below.

Table 4. Rate Constants for the Reaction of OH Radicals with a Series of Cycloalkenes at 298 ± 2 K

Cycloalkene	10^{11} x k (cm^3 $molecule^{-1}$ s^{-1})[a]
Cyclopentene	6.70 ± 0.24
Cyclohexene	6.74 ± 0.17
Cycloheptene	7.41 ± 0.23
1,3-Cyclohexadiene	16.3 ± 0.5
1,4-Cyclohexadiene	9.94 ± 0.41
Bicyclo[2.2.1]-2-heptene	4.91 ± 0.40
Bicyclo[2.2.1]-2,5-heptadiene	12.0 ± 1.0
Bicyclo[2.2.2]-2-octene	4.06 ± 0.19

[a]Indicated error limits are two least squares standard deviations.

Table 5. Rate Constants for the Reactions of Ozone and OH Radicals with a Series of Alkynes at Room Temperature[a]

Alkyne	$10^{20} \times k^{O_3}$ (cm^3 $molecule^{-1}$ s^{-1})	$10^{12} \times k^{OH}$ (cm^3 $molecule^{-1}$ s^{-1})
Acetylene	0.78 ± 0.12	0.86 ± 0.14
Propyne	1.43 ± 0.15	6.06 ± 0.30
1-Butyne	1.97 ± 0.26	8.04 ± 0.23

[a]The error limits are two standard deviations.

Table 6. Rate Constants k at 297 ± 2 K for the Reaction of OH Radicals with a Series of Branched Alkanes

Alkane	$10^{12} \times k$ (cm^3 $molecule^{-1}$ s^{-1})[a]
Isobutane	2.22 ± 0.06
2-Methylbutane	3.87 ± 0.10
2,2-Dimethylbutane	2.59 ± 0.08
2-Methylpentane	5.52 ± 0.23
3-Methylpentane	5.62 ± 0.10
2,2,3-Trimethylbutane	4.09 ± 0.08
2,4-Dimethylpentane	5.12 ± 0.10
Methylcyclohexane	10.3 ± 0.3
2,2,3,3-Tetramethylbutane	1.03 ± 0.08
2,2,4-Trimethylpentane	3.56 ± 0.15

[a]The indicated errors are two least squares standard deviations.

• Rate constants for the reaction of O_3 with naphthalene and biphenyl, and of OH radicals with naphthalene, biphenyl and 2-, 3- and 4-chlorobiphenyl were determined at 295 K. Because of the relatively low volatilities of these aromatics, experiments were carried out in the SAPRC ~6400 liter all-Teflon environmental chamber. The data obtained are given in Table 7 and discussed in detail by Atkinson et al. (1984a) and Atkinson and Aschmann (1985).

Table 7. Rate Constants for the Reaction of O_3 and OH Radicals with Naphthalene, Biphenyl and the Monochlorobiphenyls at ~295 K

	$10^{19} \times k^{O_3}$ (cm^3 $molecule^{-1}$ s^{-1})	$10^{12} \times k^{OH}$[a] (cm^3 $molecule^{-1}$ s^{-1})
Naphthalene	<2	23.3 ± 1.6
Biphenyl	<2	7.76 ± 0.68
		8.2 ± 0.8
2-Chlorobiphenyl		2.8 ± 0.4
3-Chlorobiphenyl		5.2 ± 0.8
4-Chlorobiphenyl		3.8 ± 0.7

[a]Error limits are two standard deviations.

• In order to obtain further data for conjugated dialkenes and for trialkenes, the O_3 and OH radical reaction rate constants for 1,3-cycloheptadiene, 1,3,5-cycloheptatriene and cis- and trans-1,3,5-hexatriene, and of O_3 with cis-2, trans-4- and trans-2, trans-4-hexadiene were determined at 294 ± 2 K. The rate constants obtained are given in Table 8 and are discussed by Atkinson et al. (1984c).

• Rate constants for the reaction of OH radicals with a series of alkenes and dialkenes were determined at 295 ± 1 K to provide a self-consistent data set. n-Butane and n-hexane were also studied to provide a cross-check of the kinetic data sets for the alkanes and alkenes. The rate constants obtained are given in Table 9 and discussed in detail by Atkinson and Aschmann (1984b).

• The O_3 and OH radical reaction rate constants for diacetylene were determined at 297 ± 2 K. The rate constants obtained were:

$$k^{O_3} = (6^{+4}_{-3}) \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

and

$$k^{OH} = (1.57 \pm 0.06) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}.$$

This study, and the results obtained, are discussed in detail by Atkinson and Aschmann (1984c).

Table 8. Rate Constants for the Reaction of O_3 and OH Radicals with a Series of Dialkenes and Trialkenes at 294 ± 2 K

	$10^{16} \times k^{O_3}$ (cm^3 $molecule^{-1}$ s^{-1})[a]	$10^{11} \times k^{OH}$ (cm^3 $molecule^{-1}$ s^{-1})[a]
1,3-Cycloheptadiene	1.56 ± 0.21	13.9 ± 0.4
1,3,5-Cycloheptatriene	0.539 ± 0.078	9.74 ± 0.25
cis-1,3,5-Hexatriene	0.262 ± 0.034[b]	11.1 ± 0.8
trans-1,3,5-Hexatriene		11.2 ± 1.8
cis-2, trans-4-Hexadiene	3.14 ± 0.34	
trans-2, trans-4-Hexadiene	3.74 ± 0.61	

[a]Errors are two least squares standard deviations.
[b]cis- and trans-isomers have identical rate constants, to within ~±10%.

Table 9. Rate Constants for the Reaction of OH Radicals with a Series of Alkenes and Dialkenes and n-Butane and n-Hexane at 295 ± 1 K

	$10^{12} \times k^{OH}$ (cm^3 $molecule^{-1}$ s^{-1})[a]
Ethene	8.66 ± 0.40
Propene	(26.8)[b]
1-Butene	31.9 ± 1.6
1-Pentene	31.9 ± 1.4
1-Hexene	37.5 ± 1.1
1-Heptene	40.5 ± 1.6
3-Methyl-1-butene	32.4 ± 1.1
2-Methylpropene	52.3 ± 2.4
cis-2-Butene	57.1 ± 1.4
trans-2-Butene	65.1 ± 1.4
2-Methyl-2-butene	88.4 ± 3.5
2,3-Dimethyl-2-butene	112 ± 5
Propadiene	9.84 ± 0.97
1,3-Butadiene	67.8 ± 2.2
2-Methyl-1,3-butadiene	102.1 ± 4.0
n-Butane	2.71 ± 0.32
n-Hexane	5.31 ± 0.46

[a]Error limits are two least squares standard deviations.
[b]Reference organic.

The experimental data obtained from these kinetic studies provided a large amount of important new data, and allowed the development of a-priori predictive techniques for a large number of classes of organic compounds. These data were incorporated into the major tasks of this cooperative agreement, namely the critical evaluation and review of OH radical and O_3 reactions.

4. REVIEW AND EVALUATION OF OH RADICAL AND O_3 REACTION RATE CONSTANTS

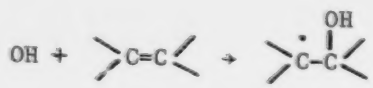
In the two review articles "Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds under Atmospheric Conditions" and "Kinetics and Mechanisms of the Gas Phase Reactions of the Hydroxyl Radical with Organic Compounds under Atmospheric Conditions" the available kinetic product and mechanistic data for the gas phase reactions of O_3 and of OH radicals with organic compounds were compiled, evaluated and reviewed. Emphasis was placed upon the kinetics and mechanisms of these reactions under atmospheric conditions. Thus kinetic data obtained at low total pressures where the reactions of OH radicals with certain of the alkenes, haloalkenes, alkynes and aromatic hydrocarbons are in the fall-off regime between second- and third-order kinetics were not considered. In a similar manner, high temperature ($\gtrsim$500 K) data were not included in these reviews unless these data had been obtained in investigations carried out over temperature ranges extending to $\lesssim$500 K. In the following section, discussions, excerpted from these two review articles, dealing with rate constant trends and correlations and with a-priori predictions of room temperature rate constants are given.

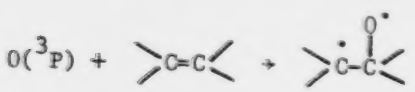
Ozone Reactions

Rate Constant Trends and Correlations

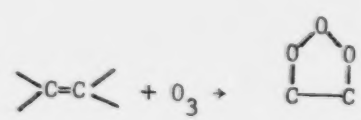
Kinetic data are available for the reactions of O_3 with a variety of organics. For certain classes of organics, these data allow possible rate constant trends and correlations to be examined. The great majority of organics for which kinetic data are available, and which react with O_3 at sufficiently high rates to be of possible atmospheric significance, contain unsaturated carbon-carbon bonds (i.e., C=C or C≡C bonds), with the initial reaction involving O_3 addition across these unsaturated carbon-carbon bonds. However, certain nitrogen-containing compounds (such as the amines, hydrazines, diazo compounds, and hydrazones), and possibly certain organometallics, also react with O_3 at significant rates, apparently via different mechanisms than for those organics containing C=C or C≡C bonds. Unfortunately, the available kinetic data for these latter classes of organics are insufficient to allow any meaningful discussion of rate constant correlations and trends, and hence in this section discussion is restricted to organics containing unsaturated carbon-carbon bonds.

Correlations with OH Radical and $O(^3P)$ Atom Rate Constants. O_3 is electrophilic in character, as are $O(^3P)$ atoms, OH radicals and NO_3 radicals, and it may thus be expected that the rate constants for the addition reactions of these species to double and triple carbon-carbon bonds would exhibit some degree of correlation. Examples of the correlations between O_3 and OH-radical and $O(^3P)$ atom and OH radical rate constants with a series of unsaturated organics are shown in Figures 3 and 4. It can be seen from these figures that while the correlation between $O(^3P)$ atom and OH radical rate constants for these organics containing >C=C< bonds is excellent (Figure 4), that between O_3 and OH radicals is substantially more scattered (Figure 3). However, since OH radicals and $O(^3P)$ atoms both react in a closely analogous manner by initially adding to one side of the unsaturated >C=C< or -C≡C- bond, forming a radical species





(reaction of $O(^3P)$ atoms with alkenes to form the alkene oxides in a single step being spin-forbidden), while O_3 adds across the unsaturated >C=C< or -C≡C< bond to initially form a non-radical ozonide,



then these reactions are not strictly analogous. Indeed, as previously pointed out by Atkinson (1980), rate constant correlations are only accurate and useful if reactions which occur via analogous mechanisms are compared. Thus, except on a qualitative basis, and then only after the effects of conjugation and ring strain, as discussed in the following

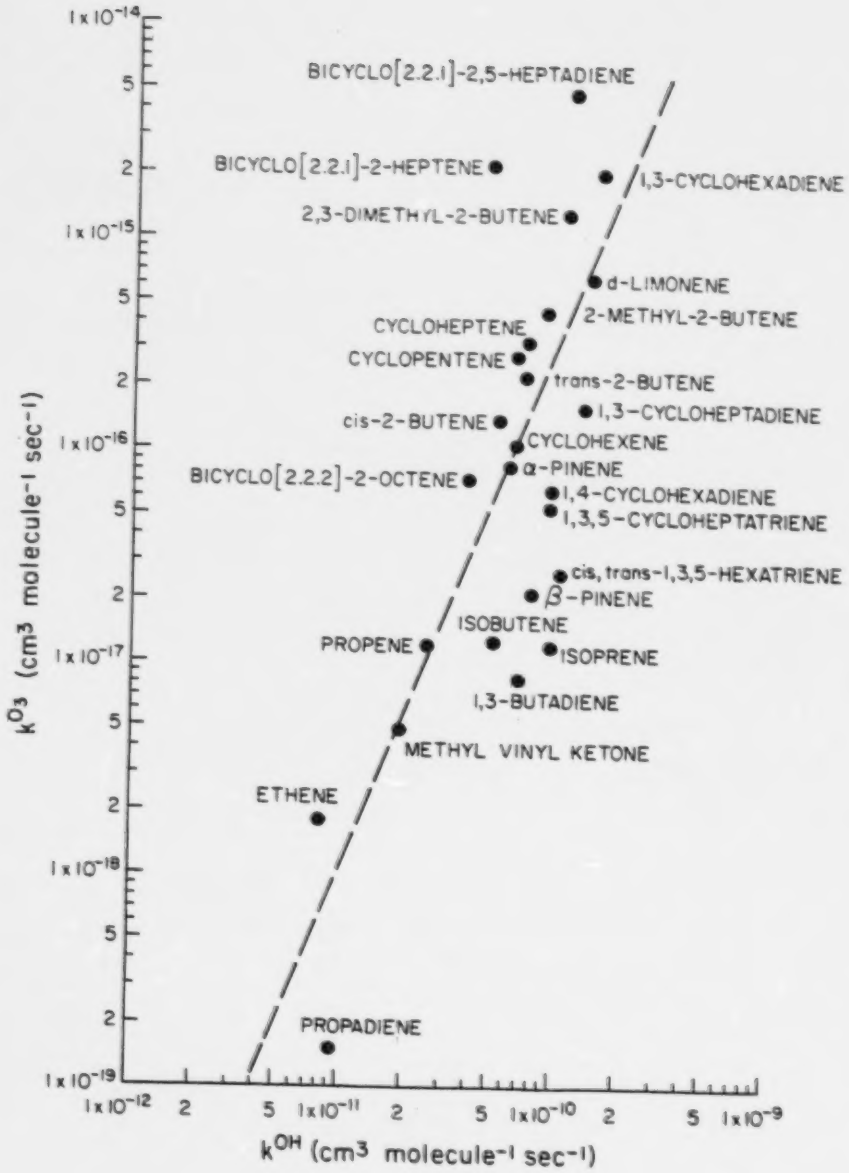


Figure 3. Plot of log $k^{O}3$ against log k^{OH} for a series of alkenes, cycloalkenes and methyl vinyl ketone at room temperature [from Atkinson (1985)].

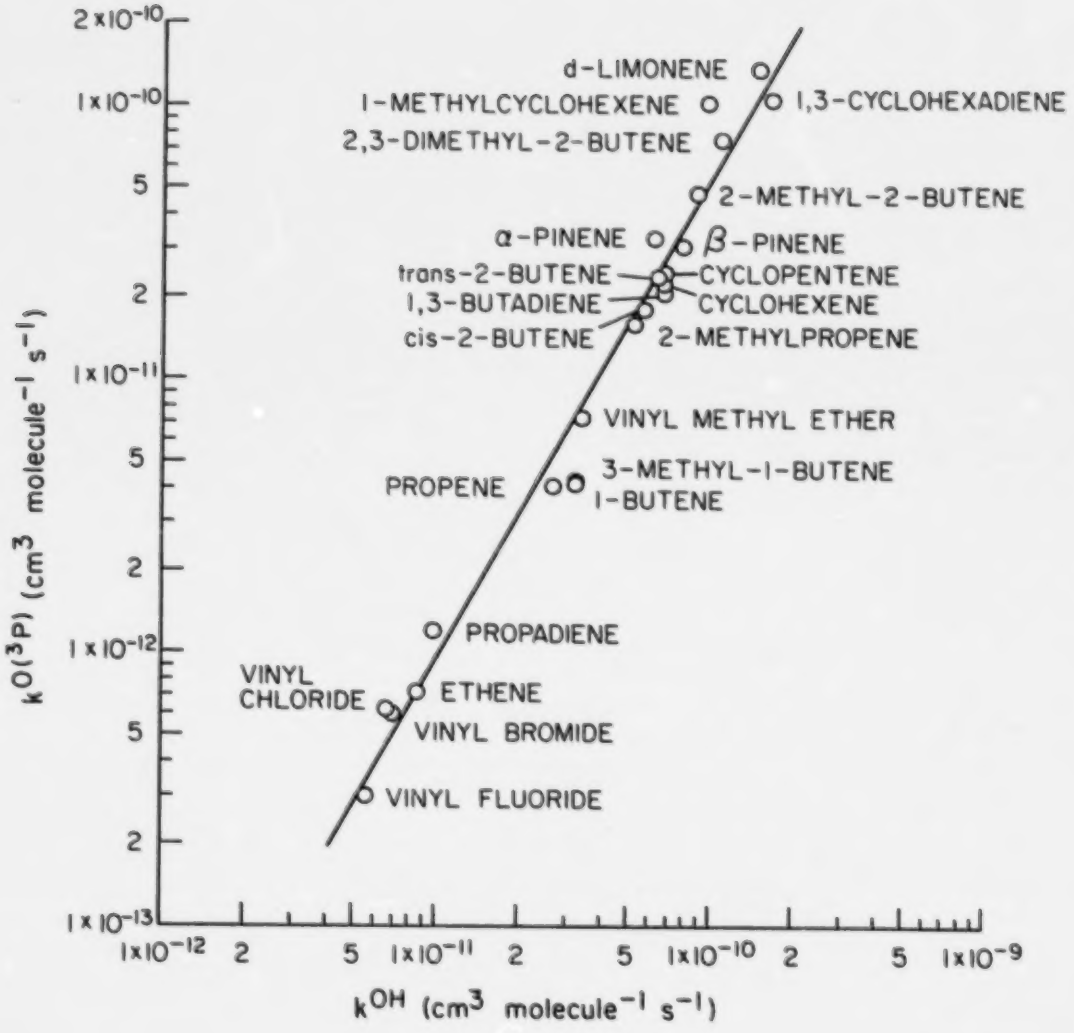


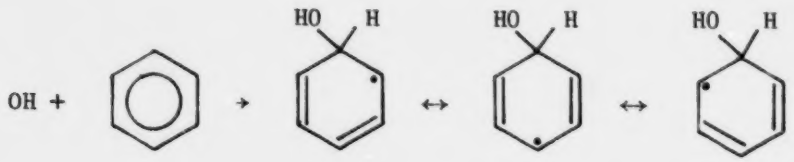
Figure 4. Plot of log $k^{O(^3P)}$ against log k^{OH} for a series of alkenes, cycloalkenes, haloalkenes and vinyl methyl ether at room temperature [from Atkinson (1985)].

sections, are taken into account, we do not recommend the use of correlations with OH radical or $O(^3P)$ rate constants to estimate rate constants for the reactions of O_3 with organics.

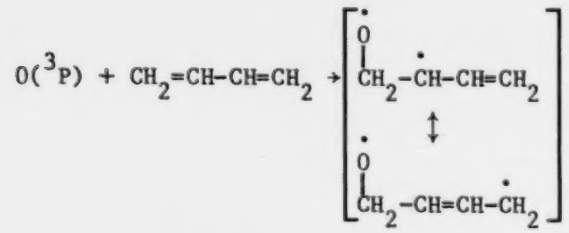
Effects of Conjugation and Aromaticity. It can be seen from Figure 3 that, except for 1,3-cyclohexadiene (discussed in the following section), the room temperature rate constants for the reaction of O_3 with conjugated di- and tri-alkenes are significantly low when compared with the O_3 reaction rate constants for the corresponding non-conjugated alkenes, and with predictions based upon correlation with the corresponding OH radical rate constants. In particular, for reaction with O_3, 2-methyl-1,3-butadiene (isoprene) is similar in reactivity to propene, 1-butene and 2-methyl-2-propene, and cis- and trans-1,3,5-hexatriene are less reactive at room temperature than the 2-butenes or the tri- and tetra-substituted ethenes, while in terms of $O(^3P)$ atom and OH radical reactions, 1,3-butadiene is of similar reactivity to trans-2-butene, 2-methyl-1,3-butadiene is of comparable reactivity to 2-methyl-2-butene, and cis- and trans-1,3,5-hexatriene are of comparable reactivity to 2,3-dimethyl-2-butene. Thus in general it can be concluded that conjugation has a more significant effect in reducing the rate constants for the reaction of O_3 with alkenes than is the case for OH radical or $O(^3P)$ atom reactions. This again can be attributed to the differing initial reactions and transition states involved.

The most extreme effects of conjugation would obviously be seen in aromatic compounds, where the large resonance stabilization energy would be expected to have a large and suppressing effect on the O_3, OH radical or $O(^3P)$ atom rate constants. The rate constants for the reactions of OH radicals and $O(^3P)$ atoms with benzene are factors of ~7 and ~40 lower, respectively, than their rate constant for reaction with ethene (Atkinson et al. 1979); while O_3 reacts with benzene over four orders of magnitude slower than it does with ethene. The relatively low rate constant for the reaction of O_3 with furan is consistent with this effect, since furan also has some aromatic character. This extreme effect of aromaticity in suppressing O_3 rate constants is consistent with, and can be considered to be an extension of, the negative effects of conjugation on these rate constants.

The fact that conjugation and resonance stabilization have much larger effects on suppressing O_3 rate constants than on the corresponding OH radical or $O(^3P)$ atom rate constants can be attributed to the fact that while in all three systems resonance (or conjugation) stabilization is lost or reduced in the transition state, the radical (or biradical) formed in the reaction of OH radicals or $O(^3P)$ atoms with aromatics or conjugated alkenes remains resonance stabilized, compensating for the loss of aromaticity or reduction of conjugation stabilization in the transition state: e.g.,



and

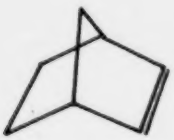


However, since an analogous stabilization of the molecular ozonide intermediate form in the initial O_3 reaction cannot occur, there is no compensation for the loss of aromaticity or conjugation stabilization in the initial reaction, and thus the effects of conjugation or aromaticity on suppressing the rate constant are much larger.

Effects of Ring Strain. A further reason for the relatively poor correlation between O_3 and OH radical rate constants, at least for the cycloalkenes, appears to be due to the differing effects of ring strain on the kinetics of these reactions. While ring strain effects on OH radical rate constants with cycloalkenes appear to be negligible or minor (Atkinson et al. 1983d), Atkinson et al. (1983c) have shown that ring strain has a significant effect on the rate constants for the reactions of O_3 with a series of cycloalkenes and non-conjugated cyclodialkenes. We have also shown that the rate constant per double bond

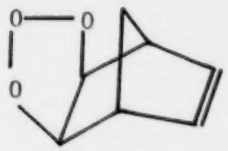
correlated better with the difference in the ring strain energy between the cycloalkene and the corresponding structure with one less double bond (i.e., the "relative" strain energy) than with the strain energy released when the bond is totally broken. For example, for bicyclo[2.2.1]-2,5-heptadiene [(I), below] the rate constant appears to be more influenced by the difference in strain energy between (I) and (II) than the strain energy difference between (I) and (III).

(I)



(II)

(III)



(IV)

Such a correlation is in accord with current mechanistic theories that these O_3 addition reactions proceed via formation of a 1,2,3-trioxide ring intermediate [Structure (IV)], since the difference between the ring strain energy of the 1,2,3-trioxide (IV) and (II) should be approximately independent of the cycloalkene or non-conjugated cyclodialkene being studied, since the strain energies of polycyclic ring compounds are approximately the sum of the strain energies of the individual rings (Benson 1976).

It is interesting that O_3 reacts with 1,3-cyclohexadiene ~6 times faster than with its acyclic analogue 2,4-hexadiene, and with 1,3-cycloheptadiene a factor of ~2 slower than with 2,4-hexadiene. While this order-of-magnitude difference in the rate constants between 1,3-cyclohexadiene and 1,3-cycloheptadiene could be due in part to the fact that 1,3-cycloheptadiene has a slightly higher relative strain energy (Benson 1976, Atkinson et al. 1984c), the magnitude of the difference suggests that other factors may also be involved. It should also be noted that the rate constant for the reaction of O_3 with 1,3,5-cycloheptatriene is even lower than that for 1,3-cycloheptadiene, by a factor of ~3, despite the fact that 1,3,5-hexatriene reacts with O_3 a factor of ~3 faster than does 1,3-butadiene (Atkinson et al. 1984c). This could also be due in part to the effect of relative ring strain, since 1,3,5-cycloheptatriene is

estimated to have a negative relative strain energy of ~-2 kcal $mole^{-1}$ (Benson 1976), but this cannot be accurately assessed because the rate constant for its acyclic analogue, 2,4,6-octatriene, is not known. Obviously, additional data are required to more unambiguously assess the combined effects of ring strain and conjugation on the rate constants for the reaction of O_3 with cyclo-dialkenes and trialkenes.

Substituent Effects. Based upon the data given by Atkinson and Carter (1984), the most important single factor in determining how rapidly O_3 reacts with a carbon-carbon double bond is the nature, number, and orientation of substituents around that bond. The available data concerning these effects are summarized in Table 10, where the factors by which the room temperature O_3 rate constant is changed when one or more H-atoms on ethene are replaced by various substituents for which data are available are given. (The effects of substitution by ethyl and larger alkyl groups are not shown since the data are limited and these effects appear to be similar to $-CH_3$ substitution). It can be seen that some substituents, such as phenyl, methyl (and higher alkyl groups) and acetyl groups tend to enhance the room temperature O_3 reaction rate constants, whereas others, such as formyl, chloromethyl, cyano, chloro, and fluoro substituent groups tend to suppress the O_3 reaction rate constant. In general, as expected, electron-withdrawing substituents tend to suppress the rate constants, while electron-donating substituents such as methyl or other alkyl groups tend to enhance the rate constant. This effect is totally consistent with the electrophilic nature of O_3 as a reactant towards >C=C< and >C≡C< bonds. As further shown in Table 11, replacement of an H-atom by a -CHO group on an olefinic double bond decreases the room temperature O_3 reaction rate constant by a factor of ~8±2, while replacement of an H-atom by a $-COCH_3$ group increases the rate constant by a factor of ~2-3.

In terms of the effects of number and orientation of substituents about olefinic double bonds, the only complete and reliable data set concerns the effects of alkyl substituents. However, less reliable, and in some cases only upper-limit, data concerning the effects of Cl- and F-atom substitution are also available. Although, as shown in Table 10 and Figure 5, the enhancement of the rate constant due to alkyl substitution increases with the number of substituents, it does not increase in a

Table 10. Effects of Substituent Identity, Number, and Orientation About the Carbon-Carbon Double Bond on Room Temperature Rate Constants for the Reaction of O_3 with Organics, Relative to the Room Temperature Rate Constant for the Reaction of O_3 with Ethene

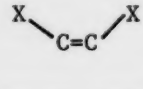
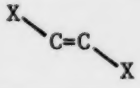
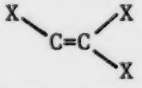
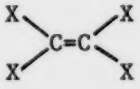
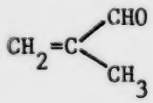
Substituent (-X)	Number and Orientation					
						
$-C_6H_5$	12					
$-CH_3$	6.5	6.9	74	114	240	660
$-COCH_3$	2.7		1.0	4.7		
-CHO	0.16					
$-CH_2Cl$			0.22			
-CN	<0.1					
-F	0.4	<0.11	0.15	1.2	0.014	0.29
-Cl	≤0.004	0.002	<0.003	≤0.2	≤0.02	<0.00001

Table 11. Effect of Substituent -CHO and CH_3CO- Groups on Room Temperature O_3 Reaction Rate Constants

Carbonyl	10^{18} x k (cm^3 $molecule^{-1}$ s^{-1})[a]	Alkene	10^{18} x k (cm^3 $molecule^{-1}$ s^{-1})[b]	Substituent Effect
CH_2=CHCHO	0.28	CH_2=CH_2	1.75	0.16
CH_3CH=CHCHO	0.90	CH_3CH=CH_2	11.3	0.08
	1.12	CH_2=$CHCH_3$	11.3	0.10
CH_3COCH=CH_2	4.77	CH_2=CH_2	1.75	2.7
CH_3COCH=$CHCH_3$	21.3	CH_2=$CHCH_3$	11.3	1.9

[a]From Atkinson et al. (1981).
[b]From the recommendations of Atkinson and Carter (1984) for the alkenes at 298 K.

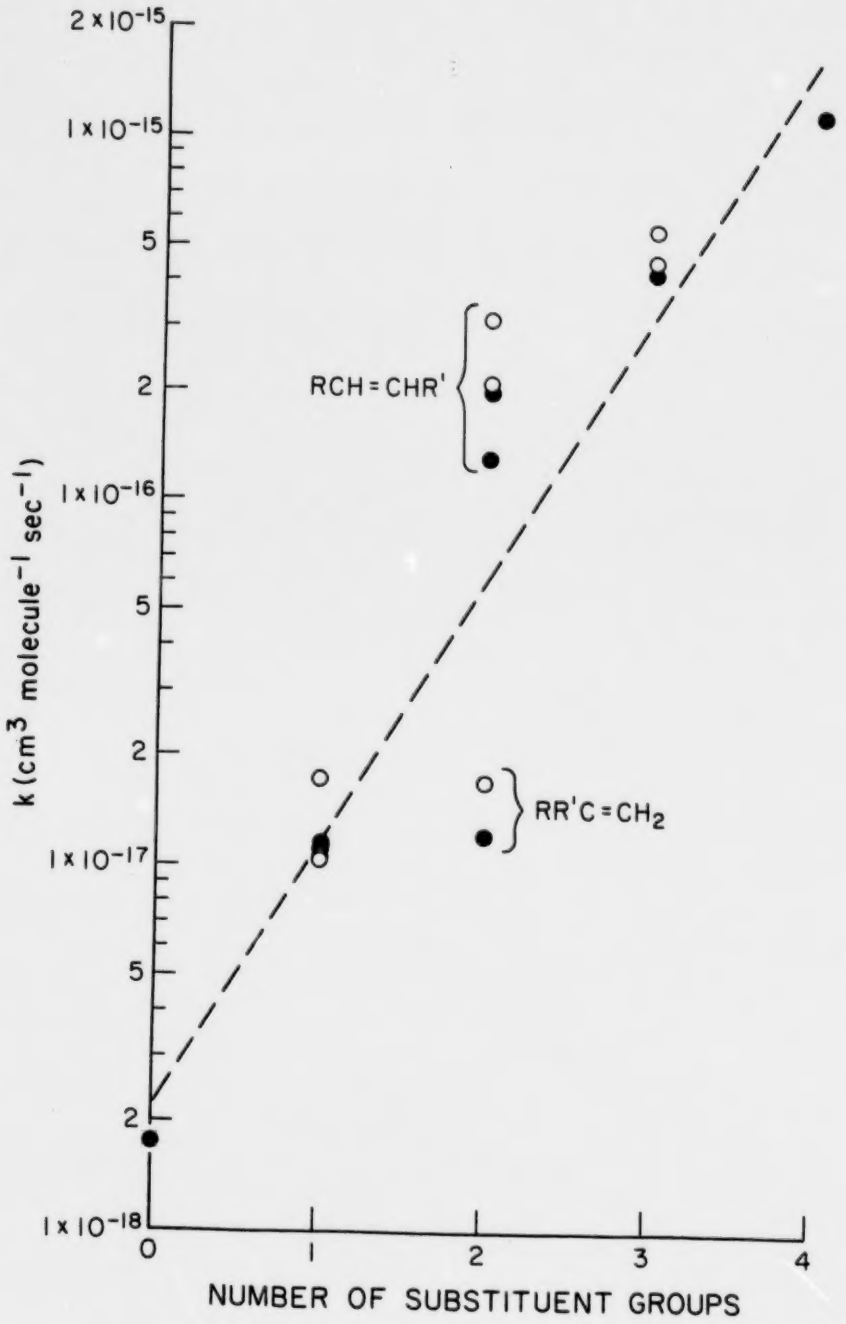


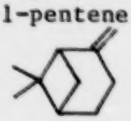
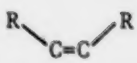
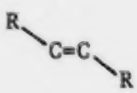
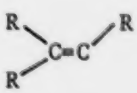
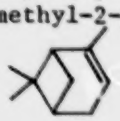
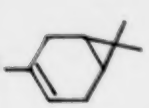
Figure 5. Plot of the room temperature rate constants for the reaction of O_3 with ethene and alkyl-substituted ethenes against the number of alkyl substituents [from Atkinson and Carter (1984)]. (●) Alkenes for which recommended rate constants were given; (○) alkenes for which insufficient data are available for recommendations to be given.

simple proportional manner, and for the two-substituent case the effect of orientation around the olefinic double bond is significant with the trans-1,2-isomer being significantly more reactive than the cis-1,2-isomer. In particular, the terminal alkenes $RR'C{=}CH_2$ are an order of magnitude less reactive than are the internal alkenes RCH=CHR'. This situation is different to that for $O(^3P)$ atom and OH radical reactions, for which the rate constants increase monotonically with the degree of substitution around the olefinic double bond (Atkinson et al. 1979). The effects of orientation for the disubstituted alkenes are also important for the diones and the haloalkenes, with the internal dihaloalkenes reacting faster than the terminal dihaloalkenes, and with the trans-1,2-dihalo or the trans-3-hexene-2,5-dione isomers reacting appreciably faster than the corresponding cis-isomers. Further evidence for a large cis- vs trans-effect comes from the room temperature rate constants for the reactions of O_3 with the 1,3-dichloropropenes (Tuazon et al. 1984a), where the rate constant for the trans-isomer is a factor of ~4.5 higher than that for the cis-isomer. There is no obvious explanation for this effect, except to note that steric factors may to some extent be contributing.

Estimation of O_3 Reaction Rate Constants

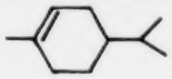
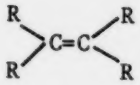
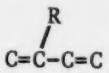
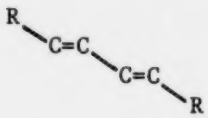
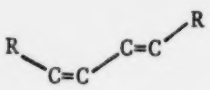
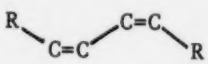
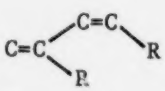
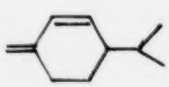
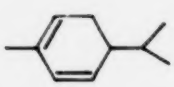
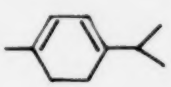
Alkenes with Single or Non-Conjugated Double Bond Systems. The rate constants for the acyclic alkenes and non-conjugated dialkenes indicate that to a first approximation the room temperature rate constants are determined by the degree and configuration of alkyl substitution about the double bond, and not by the precise identity of the alkyl substituent. This is also expected to hold for cycloalkenes with relatively low-strain 6-member rings. By analogy, for conjugated acyclic dialkenes the rate constant is anticipated to be determined mainly by the degree and configuration of alkyl substitution about the C=C-C=C bond system, although data are available for only a few of the many possible configurations. This suggests an obvious technique for estimation of O_3 rate constants for this class of organics, based on our recommended rate constants for the simplest representative alkenes. These recommendations for alkenes with varying degrees and configurations of alkyl substitution are given in Table 12, together with the experimental data for the more complex alkenes, and these can be compared with the "estimated" values.

Table 12. Summary of Estimated Room Temperature O_3 Rate Constants for Acyclic Alkenes or Unstrained Cycloalkenes with Varying Degrees and Configuration of Alkyl Substitution, Compared with Experimental Data

General Structure	10^{16} x k (estimated) (cm^3 $molecule^{-1}$ s^{-1})	Alkene	10^{16} x k (observed[a]) (cm^3 $molecule^{-1}$ s^{-1})
R-C=C	0.12	propene	0.11[b]
		1-butene	0.11[b]
		1-pentene	0.05-0.11
		1-hexene	0.12[b]
		1-heptene	0.08-0.17
		1-octene	0.08
		1-decene	0.11
		4-methyl-1-pentene	0.11
	0.12	2-methyl-2-propene	0.12[b]
		2-methyl-1-pentene	0.17
		β-pinene 	0.21-0.36
	1.3	cis-2-butene	1.30[b]
		cis-2-pentene	2.1
		cyclohexene	0.6-2.0
	2.0	trans-2-butene	2.0[b]
		trans-2-pentene	3.2
	4.3	2-methyl-2-butene	4.2[b]
		cis-3-methyl-2-pentene	4.6
		trans-3-methyl-2-pentene	5.6
		α-pinene 	0.83-3.3
		Δ^3-carene 	1.2

(continued)

Table 12 (continued) - 2

General Structure	10^{16} x k (estimated) (cm^3 $molecule^{-1}$ s^{-1})	Alkene	10^{16} x k (observed[a]) (cm^3 $molecule^{-1}$ s^{-1})
		carvomethene 	5.2
	12	2,3-dimethyl-2-butene	11.6[b]
	0.14	isoprene	0.143[b]
	3.7	trans-2, trans-4-hexadiene	3.7
	3.1	cis-2, trans-4-hexadiene	3.1
	~3[c]	1,3-cyclohexadiene	19.7
	0.14-3[d]	β-phellandrene 	1.8
$(C=C-C=C)-R_3$	>3	α-phellandrene 	120
$(C=C-C=C)-R_4$	>>3	α-terpinene 	880

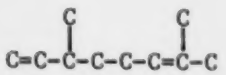
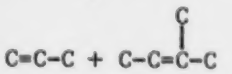
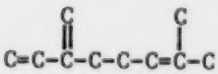
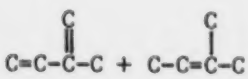
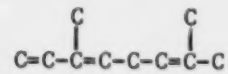
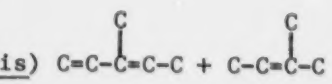
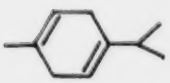
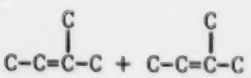
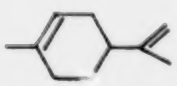
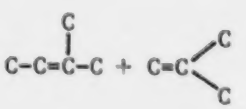
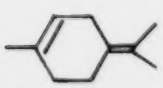
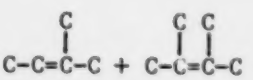
[a] Unless indicated otherwise, the range of values available is given. The appropriate tables should be consulted for references.
[b] Recommended value.
[c] Assumed to be the same as the cis-, trans-isomer.
[d] Assumed to be between the rate constants for isoprene and the 2,4-hexadienes.

It can be seen from Table 12 that this estimation technique works reasonably well for the monoalkenes, including the six-membered cycloalkenes, with the possible exceptions of α- and β-pinene and Δ^3-carene, where ring strain effects may be non-negligible. For the acyclic conjugated dialkenes, insufficient data are available to test this technique, though based on the poor agreement between the observed and estimated rate constants for 1,3-cyclohexadiene it does not appear to be particularly useful for the cyclodialkenes. While no data are available for the dialkenes with the same number and orientation of substituents as those in α- and β-phellandrene and α-terpinene, the observed rate constants are consistent with our estimates of the lower limit values.

For alkenes with non-conjugated double bonds (including alkenes with both conjugated and non-conjugated double bond systems), it may be anticipated that the rate constants per nonconjugated double bond or conjugated double bond system are additive [as appears to be the case for OH radical reactions (Atkinson et al. 1983d)], with the rate constant for each system being that for the simpler alkenes with the same degree and configuration of alkyl substitution around the double bonds. Kinetic data against which this assumption can be tested are available primarily from the study of Grimsrud et al. (1975) for the reaction of O_3 with a number of acyclic and cyclic monoterpenes having separated double bond systems. Table 13 shows a comparison of the observed rate constants for these monoterpenes with the rate constants so estimated, together with the structures of the simpler alkenes used to derive the estimated rate constants.

It can be seen from Table 13 that the agreement between the estimated and observed rate constants is good to within approximately a factor of 2-3. For terpinoline, the estimated rate constant is consistent only with the lower of the two reported measurements, and suggests that the rate constant determined by Grimsrud et al. (1975) may be in error. Obviously additional measurements of these rate constants are clearly desirable in order to more unambiguously test this estimation technique. However, this agreement to within a factor of ~3, with the possible exception of terpinoline, suggests that for acyclic alkenes or cycloalkenes with only low strain six-membered rings the room temperature rate constants can be approximately estimated based on the number of double bonds or conjugated

Table 13. Comparison of Measured and Estimated Room Temperature Rate Constants for the Reaction of O_3 with Di- and Tri-Alkenes with Non-Conjugated Double Bond Systems

Name and Structure	Structures for Compounds used to Estimate k	10^6 x k(cm^3 $molecule^{-1}$ s^{-1}) Estimated[a]	Observed[b]
 (Dihydromyrcene)		4.4	6.8
 (Myrcene)		4.4	12.5
(cis)  (Ocimene)	(cis) 	4.4-7.3[c]	20
 (γ-Terpinene)		8.4	2.8
 (d-Limonene)		4.4	6.4
 (Terpinolene)		15	7[d], 100

[a] Estimated based on recommended values for compounds listed in second column.
[b] Except as noted, from Grimsrud et al. (1975).
[c] The rate constant for cis-3-methyl-1,3-pentadiene is not known, but is expected to be between that for 2-methyl-1,3-butadiene (isoprene) and the 2,4-hexadienes.
[d] From Japar et al. (1974).

double bond systems and the degree and configuration of substitution around these double bond systems.

Organics with More than One Type of Substituent. A more difficult problem is the estimation of O_3 rate constants for organics with more than one type of substituent on the carbon-carbon double bond. This problem is difficult not only because of the limited data available concerning the effects of multiple substituents other than for alkyl groups, but also because of the even more limited number of compounds which have more than one type of substituent for which kinetic data are available, and which can be used to test estimation techniques. In particular, other than the two 1,3-dichloropropene isomers, the only mixed-substituent compounds which have been studied to date are methacrolein, crotonaldehyde, and 2-pentene-2-one, which have both CH_3-, and either -CHO or $-COCH_3$ substituent groups about the carbon-carbon double bond. However, these latter three compounds can be used to explore the utility of simple estimation techniques.

One obvious way to estimate rate constants for reactions of compounds with more than one type of substituent is to start with the room temperature rate constant for the reaction of O_3 with ethene, and to assign to each substituent the multiplicative factor by which addition of the substituent changes the ethene rate constant (tabulated in the first column in Table 10). Thus, for example, for both crotonaldehyde and methacrolein, the ethene rate constant would be multiplied by 6.5 (for $-CH_3$) and by 0.16 (for -CHO) to obtain the estimated rate constant. This technique is simple, data are available concerning the (enhancement/suppression) factors for a number of substituents (Table 10), and it can readily be tested against compounds with multiple numbers of the same substituents. Table 14 compares the experimental room temperature O_3 rate constant reactions for the di-, tri-, and tetra-methyl substituted ethenes, the haloalkenes and for the three mixed-substituent oxygenates listed above against the rate constants estimated in this manner (indicated as method A in this table). It can be seen that, except for isobutene, cis-3-hexene-2,5-dione, and certain of the haloalkenes, the estimated and experimental rate constants agree to within a factor of 3, which can be considered to be good considering the simplicity of this technique.

Table 14. Comparison of Observed and Estimated Room Temperature O_3 Rate Constants for Selected Organics with Multiple Substituents Around the Carbon-Carbon Double Bond

Organic	10^{18} x k(cm^3 $molecule^{-1}$ s^{-1})		
	Observed	Estimated	
		Method A[a]	Method B[a]
$CH_2=C(CH_3)_2$	12	74	-
cis-$CH_3CH=CHCH_3$	130	74	-
trans-$CH_3CH=CHCH_3$	200	74	-
$(CH_3)_2C=CHCH_3$	423	480	-
$(CH_3)_2C=C(CH_3)_2$	1160	3100	-
$CH_2=C(CH_3)CHO$	1.12	1.8	0.30
trans-$CH_3CH=CHCHO$	0.90	1.8	4.9
$CH_3CH=CHCOCH_3$ (30% cis, 70% trans)	21.3	31	54-83
cis-$CH_3COCH=CHCOCH_3$	1.8	13	22
trans-$CH_3COCH=CHCOCH_3$	8.3	13	35
$CH_2=CCl_2$	0.25-0.65	0.036	0.0058
cis-CHCl=CHCl	0.062	0.036	0.063
trans-CHCl=CHCl	0.18-0.38	0.036	0.097
$CHCl=CCl_2$	<0.03	0.005	0.0045
$CCl_2=CCl_2$	<0.00002	0.0007	0.00027
$CH_2=CF_2$	0.19	0.28	0.045
cis-CHF=CHF	0.26	0.28	0.49
trans-CHF=CHF	2.1	0.28	0.76
$CHF=CF_2$	0.14	0.11	0.099
$CF_2=CF_2$	0.092	0.045	0.017

[a]Calculated for the chloroethenes using the rate constant of Zhang et al. (1983) for vinyl chloride.

An alternate estimation technique for the mixed-substituent organics, which takes into account to some extent the effects of substituent configuration, utilizes the O_3 rate constant for the methyl-substituted ethene with the same degree and configuration of methyl substituents about the carbon-carbon double bond as the substituents (of all types) in the subject organic, and for each substituent (other than methyl) to multiply the rate constant by the (enhancement/suppression) factor for that substituent, divided by the enhancement factor for methyl (first column of Table 10). Thus the O_3 rate constant for methacrolein is estimated by multiplying the isobutene rate constant by 0.16 (for -CHO) and dividing by 6.5 (for $-CH_3$), and likewise the rate constant for crotonaldehyde (which exists in the trans form) is obtained by multiplying the trans-2-butene rate constant by the same factors. The rate constants estimated in this way for the three mixed-substituent oxygenates, the 3-hexene-2,5-dione isomers, and the haloalkenes are indicated in Table 14 (as method B), where they can be compared with the estimates using Method A and the experimental data.

It can be seen that this second technique (Method B) does not predict the rate constants for these three mixed-substituent oxygenates and the 3-hexene-2,5-dione isomers quite as well as does the first, more simplistic method (A). In particular, Method B predicts that, since O_3 reacts much more rapidly with trans-2-butene than it does with isobutene, then the same would be the case for crotonaldehyde compared to methacrolein, contrary to the experimental data which shows that they both have similar rate constants. However, the trans-1,2-dihaloethenes do react significantly more rapidly with O_3 than do the cis-isomers and Method B is indeed somewhat more successful in predicting rate constants for these organics. However, in general it appears that the simplest technique (Method A) should be used for the estimation of O_3 rate constants for organics for which no experimental data are available. Clearly, much more data are required, including in particular temperature dependence studies in order that steric and energetic factors can be considered separately, before reliable estimation techniques for mixed-substituent organics can be developed.

Conclusions

As discussed by Atkinson and Carter (1984), a large number of kinetic studies have been carried out with a variety of organics, allowing estimates of atmospheric lifetimes to be obtained. However, as discussed above, insufficient data are presently available to allow reliable estimates of O_3 rate constants, and thus atmospheric lifetimes, for organics for which no experimental data are presently available, with the possible exceptions of the simple alkenes, certain di- and tri-alkenes with separated double bond systems and certain haloalkenes. In addition, only for a few simple alkenes are reliable temperature dependence data available. Finally, it should be noted that major uncertainties exist concerning the mechanism of the reaction of O_3 with essentially all classes of organics except the simple alkenes under atmospheric conditions, and again the details are only well established for ethene itself. Thus although there exists a large body of data available concerning the atmospheric reactions of O_3 with organics, it is clear that further studies are called for, and such studies would have both theoretical and applied significance.

OH Radical Reactions

Correlations Involving OH Radical Rate Constants

A number of correlations between OH radical reaction rate constants and physical or chemical properties of the organic reactants have been investigated.

Thus, for example, OH radical addition reaction rate constants have been observed to correlate well with the ionization potential for unsaturated (Gaffney and Levine 1979, Rinke et al. 1981, GÜsten et al. 1984), and saturated (GÜsten et al. 1984) organics, including polycyclic aromatic hydrocarbons (Biermann et al. 1985). Furthermore, for aromatic compounds the OH radical rate constants for addition to the ring correlate well with the Hammett electrophilic substituent constants, σ^+ (Zetzsch 1982, Atkinson et al. 1985a). Clearly, as discussed in detail in these references, these predictive techniques are of great utility in the a-priori prediction of OH radical addition rate constants. In particular, the correlation between the room temperature rate constants for the addition of OH radicals to aromatic compounds and the electrophilic substituent constants of Brown and Okamoto (1958) is used below in our

development of an a-priori predictive scheme for OH radical rate constants with organic compounds.

For OH radical reactions which proceed via H-atom abstraction, the most used correlation to date has been that between the OH radical rate constant and the C-H bond dissociation energy (Greiner 1970, Darnall et al. 1978, Gaffney and Levine 1979, Heicklen 1981, Cohen 1982, Jolly et al. 1985) and the [sometimes (Nip et al. 1979)] related quantity, the C-H bond stretching frequencies γ_{C-H} (Nip et al. 1979, Martin and Paraskevopoulos 1983). The first application of this essentially a-priori predictive technique was that of Greiner (1970) who derived the rate constants for the reactions of the OH radical with a series of alkanes based upon the numbers of primary, secondary, and tertiary C-H bonds. This approach assumes that the C-H bond dissociation energies are essentially identical for all primary, secondary and tertiary C-H bonds, respectively, and that

$$k_{total} = N_{prim}\, k_{prim} + N_{sec}\, k_{sec} + N_{tert}\, k_{tert}$$

where N_{prim}, N_{sec} and N_{tert} are the numbers of primary, secondary and tertiary C-H bonds, respectively, and k_{prim}, k_{sec} and k_{tert} are the corresponding rate constants for the reaction of OH radicals with these C-H bonds. For the alkanes, the original equation due to Greiner (1970) was slightly modified by Darnall et al. (1978) to take into account more recent (through late 1978) kinetic data. This approach, though of great utility to the acyclic alkanes and the non-strained cycloalkanes (e.g., cyclohexane), is now known to be somewhat too simplistic in its assumption that all primary, secondary and tertiary C-H bonds have correspondingly identical bond dissociation energies, even within the alkanes.

In more recent such a-priori approaches to estimating (or rationalizing) H-atom abstraction rate constants by OH radicals, Atkinson (1980), Heicklen (1981), Cohen (1983), Atkinson et al. (1982b-d, 1983a, 1984b), Martin and Paraskevopoulos (1983) and Jolly et al. (1985) have extended this earlier method to take into account the dependence of differing C-H bond dissociation energies on the particular C-H bonds from which H-atom abstraction occurs. In certain of these studies, use has been made of literature C-H bond dissociation energies, while in the extensive studies of Atkinson and co-workers concerning the alkanes

(Atkinson et al. 1982b, 1983a, 1984b), ketones (Atkinson et al. 1982c) and alkyl nitrates (Atkinson et al. 1982d, 1984d), $-CH_3$, $-CH_2-$ and $>CH-$ group rate constants have been derived from the experimental kinetic data.

It has been shown [see, for example, Atkinson (1980), Heicklen (1981) and Jolly et al. (1985)] that the H-abstraction rate constant per C-H bond by OH radicals for a wide variety of organics correlates extremely well with the C-H bond dissociation energies. While similar correlations using the C-H bond stretching frequencies have been shown to apply (Nip et al. 1979, Martin and Paraskevopoulos 1983), this approach is of less utility than that employing the corresponding C-H bond dissociation energies because of the limited number of C-H bond stretching frequencies available (Jolly et al. 1985), and, in general, the complexity of this approach for any but the simpler organics (Martin and Parskevopoulos 1983).

While several of the above approaches have used literature C-H bond dissociation energies in their analyses (Atkinson 1980, Cohen 1983, Martin and Paraskevopoulos 1983, Jolly et al. 1985), Heicklen (1981) has used the available literature kinetic data to develop the following expression allowing the C-H bond dissociation energies, and hence the overall H-atom abstraction rate constants, to be estimated

$$k_{total} = \left(\frac{8\pi\ \kappa T}{\mu}\right)^{1/2} \sigma_R^2 \sum_i \gamma_i \exp\left\{\frac{-a[D_i - D_o(T)]}{RT}\right\}$$

where μ is the reduced mass, κ is Boltzmann's constant, σ_R is the reaction radius for reaction of an OH radical with a C-H bond ($\sim 1.5 \times 10^{-8}$ cm), γ_i the number of equivalent C-H bonds of each type, D_i is the C-H bond dissociation energy at 298 K for each type of C-H bond, a = 0.323, and D_o is given by

$$D_o^{-1}\ (\text{kcal mole}^{-1}) = 1.062 \times 10^{-2} + 3.52 \times 10^{-6}\ T\ (K)$$

This approach, which is one of the most general presented to date, appears to be able to yield OH radical reaction rate constants proceeding via H-atom abstraction which are reliable to within ± a factor of ~3 for the alkanes and oxygenates, but of significant less accuracy (approximately an

order of magnitude) for the haloalkanes, aromatic hydrocarbons and alkenes.

In this context, it should be noted that this general method of relating the H-atom abstraction rate constant to the C-H bond dissociation energy greatly overestimates the contribution of H-atom abstraction to the overall OH radical reaction rate constants for the alkenes and the aromatic hydrocarbons (Jolly et al. 1985), unless rather drastic and arbitrary correction factors are included (Heicklen 1981).

The more recent, and to date more restricted, approach of Atkinson et al. (see, for example, Atkinson et al. 1982b-d, 1983a, 1984b,d) has been aimed at deriving, from the experimentally observed overall rate constants, the group rate constants for H-atom abstraction appropriate to the alkanes, alkyl nitrates and ketones. While to date this technique has been more restricted in its application, it yields more accurate predictions for a given homologous series than does the more general a-priori predictive methods exemplified by that of Heicklen (1981).

Güsten et al. (1981) have proposed another predictive technique based upon the observed correlation between gas-phase and aqueous-phase OH radical rate constants, with an estimated overall uncertainty of ± a factor of ~5.

Jeong and Kaufman (1982), Jeong et al. (1984) and Cohen (1983) have derived, from transition-state theory [including tunneling effects calculated from the bond energy-bond order (BEBO) model], Arrhenius pre-exponential factors for a series of alkanes and haloalkanes. Cohen (1983) has combined these calculated Arrhenius preexponential factors with the experimental room temperature rate constants to extrapolate the existing rate constants for the reactions of the OH radical with a series of alkanes to high ($\gtrsim$2000 K) temperatures. Again, while this technique (Cohen 1983) clearly has great utility, it has to rely on either experimental or a-priori predicted rate constants at one temperature in order to "calibrate" the reaction rate constants.

Thus in these recent investigations involving the development of predictive techniques (Hendry and Kenley 1979, Heicklen 1981, Cohen 1983), reliance has been placed upon the experimental determination or the a-priori prediction of H-atom abstraction rate constants by OH radicals. The available a-priori predictive techniques for the estimation of OH

radical reaction rate constants are discussed below by the class of organic compound, and an up-to-date and extended predictive technique is presented.

Estimation of OH Radical Rate Constants

In the following sections, the available a-priori techniques advanced for the prediction of OH radical reaction rate constants with the various classes of organic compounds are discussed. At the present time these techniques have been applied to only a limited number of classes of organic compounds, and we explore below their extension to a wider variety of organic compounds.

H-Atom Abstraction from Alkanes, Carbonyls, Alkyl Nitrates and Other Unsaturated Organics. A relatively wide kinetic data base is available for the reaction of OH radicals with alkanes, haloalkanes, carbonyls, alkyl nitrates and other unsaturated organics. The following discussion of a-priori predictive techniques is analogous to that developed by Atkinson et al. (1982b-d, 1983a, 1984b,d), and is based upon the estimation of CH_3-, $-CH_2-$ and $-CH<$ group rate constants. This approach, which is analogous to the group additivity thermochemical technique of Benson (1976), is complementary to the OH radical estimation technique of Heicklen (1981) based upon measured or estimated C-H bond dissociation energies. However, the technique described by Heicklen (1981) only considers the effects of substituent groups or atoms on the α-carbon, whereas the methods of Hendry and Kenley (1979) and of Atkinson et al. (1982c) takes into account, at least in certain cases, the effects of β-substituents, although at the expense of the need for a much larger data base.

This a-priori estimation technique is based upon the premise that the $-CH_3$, $-CH_2-$ and $>CH-$ group rate constants depend on the identity of the α- and β-substituents. In the simplest case, for example in the n-alkane series, the room temperature $-CH_2-$ group rate constants are dependent on the neighboring groups, increasing from a $-CH_2-$ group bonded to two $-CH_3$ groups through a $-CH_2-$ group bonded to one $-CH_3$ and one $-CH_2-$ group to a $-CH_2-$ group bonded to two $-CH_2-$ groups (Atkinson et al. 1982b).

In the most general symbolism, these group rate constants are given by, at room temperature,

$$k(CH_3\text{-}X) = k^o_{prim}\ F(X)$$

$$k(Y\text{-}CH_2\text{-}X) = k^o_{sec}\ F(X)\ F(Y)$$

and

$$k(X\text{-}CH(Y)(Z)) = k^o_{tert}\ F(X)\ F(Y)\ F(Z)$$

where k^o_{prim}, k^o_{sec} and k^o_{tert} are the rate constants per $-CH_3$, $-CH_2-$ and >CH- groups for a given "standard" substituent, X, Y and Z are the substituent groups, and F(X), F(Y), and F(Z) are the corresponding group factors. While obviously the values of k^o_{prim}, k^o_{sec} and k^o_{tert} can be adjusted for any given substituent group X (=Y=Z), the most appropriate standard substituents are H- or CH_3- groups. For practical use, X ≡ $-CH_3$ is clearly the most useful, leading to $F(-CH_3) = 1.00$ by definition.

Using the recommended rate constants at 298 K (Atkinson 1985) together with the other available room temperature rate constants given in the relevant data tabulations, we have carried out non-linear least-squares analyses of these kinetic data, minimizing the sum of the percentage errors, to derive values of F(X) for a variety of substituent groups. Because the available kinetic data generally involve only single types of substituent groups, with few data available for difunctional and polyfunctional organics, we have analyzed the kinetic data sequentially for the various classes of organic compounds, i.e., alkanes, haloalkanes, aldehydes, carbonyls, alcohols, ethers, esters and nitrates, etc., separately. We have analyzed the more extensive data set for the alkanes to obtain k^o_{prim}, k^o_{sec} and k^o_{tert}, and $F(-CH_2-)$, F(>CH-) and F(>C<), and then used these quantities to derive values of F(X) for other substituent groups. Values of F(X), where, for example, X = $-CH_2-$, >CH-, >C<, -F, -Cl, -Br, $-CH_2F$, $-CH_2Cl$, $-CH_2Br$, $-CHF_2$, $-CHCl_2$, $-CF_3$, $-CF_2Cl$, $-CCl_3$, =O, -CHO, $-C_6H_5$, $-\overset{O}{\overset{\|}{C}}-$, $-CH_2\overset{O}{\overset{\|}{C}}-$, -O-, $-O\overset{O}{\overset{\|}{C}}-$, $-\overset{O}{\overset{\|}{C}}O-$, -OH, $-ONO_2$, and -CN are derived, as discussed below.

Alkanes. In a manner analogous to our recent study (Atkinson et al. 1984b), we have utilized our recommended room temperature rate constants for the acyclic alkanes and for cyclohexane (the sole essentially strain-free cycloalkane (Benson 1976) for which we have made a recommendation) to carry out a non-linear least-squares fit to the general equation

$$k_{total} = \Sigma[k^{o}_{prim}\ F(X)] + \Sigma[k^{o}_{sec}\ F(X)F(Y)] + \Sigma[k^{o}_{tert}\ F(X)\ F(Y)\ F(Z)]$$

As an example, the expression for 2,2,4-trimethylpentane is

$$k_{total} = 3\ k^{o}_{prim}\ F(>C<) + 2\ k^{o}_{prim}\ F\ (>CH-) + k^{o}_{sec}\ F(>C<)\ F(>CH-)$$
$$+ k^{o}_{tert} \left|F(-CH_3)\right|^2 F(-CH_2-)$$

with $F(-CH_3) = 1.00$, by definition (see above).

The values of k^{o}_{prim}, k^{o}_{sec}, k^{o}_{tert}, $F(-CH_2-)$, $F(>CH-)$ and $F(>C<)$ obtained at ~298 K are given in Table 15 and these quantities are used in our extension of this predictive approach to the other classes of organics. The experimental and predicted room temperature rate constants for the acyclic alkanes and for cyclohexane (which has essentially zero ring strain energy) are compared in Table 16. The agreement between the experimental and predicted rate constants is seen to within ±50%.

Haloalkanes. Analogous to the situation for the alkanes discussed above, we have used the values of k^{o}_{prim}, k^{o}_{sec}, k^{o}_{tert}, $F(-CH_2-)$, $F(>CH-)$ and $F(>C<)$ derived above, and the recommended room temperature rate constants for the haloalkanes (Atkinson 1985) to obtain, from a non-linear least squares analysis, the factors F(X) given in Table 15. The experimental and predicted room temperature rate constants are compared in Table 16, and again the agreement is seen to be good, typically to within ± a factor of 2, except for CHF_3 and CH_3CF_3, for which the discrepancies are factors of ~11 and ~6, respectively.

Oxygen and Nitrogen-Containing Organics. We have used the recommended room temperature rate constants for formaldehyde, acetaldehyde and 1-propanal (Atkinson 1985) to derive a value of F(=O). Since our earlier kinetic study concerning the ketones (Atkinson et al. 1982c) showed that the -CO- group affected the β-substituents as well as the α-substituents, we have used the factors $F(-\overset{O}{\overset{\|}{C}}-)$, $F(-CH_2\overset{O}{\overset{\|}{C}}-)$, $F(>CH\overset{O}{\overset{\|}{C}}-)$ and $F(>C\overset{O}{\overset{\|}{C}}-)$ in our estimation technique. Due to the limited data base available, we have assumed that $F(-CH_2\overset{O}{\overset{\|}{C}}-) = F(>CH\overset{O}{\overset{\|}{C}}-) = F(>C\overset{O}{\overset{\|}{C}}-)$ in our derivation of these factors, using our recommendations for 2-butanone, 4-methyl-2-penantone, 2,6-dimethyl-4-heptanone, and the rate constants of Atkinson et al. (1982c) for a series of ketones to derive these factors.

Table 15. Group Rate Constants, k^o, and Substituent Factors, F(X), at 298 K Derived from the Available Kinetic Data (See Text)

Group Rate Constants k^o	10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})
$k^o_{primary}$	0.143
$k^o_{secondary}$	0.821
$k^o_{tertiary}$	1.81
k^o_{-OH}	0.13[a]

Substituent Group, X	Factor F(X)
$-CH_3$	1.00[b]
$-CH_2-$, >CH-, >C<	1.30[c]
-F	0.099
-Cl	0.38
-Br	~0.30[d]
$-CH_2Cl$, $-CHCl_2$, $-CH_2Br$	0.58[e]
$-CCl_3$	~0.083[f]
$-CH_2F$	~0.85[g]

(continued)

Table 15 (continued) - 2

Substituent Group, X	Factor F(X)
$-CHF_2$	~0.10[h]
$-CF_2Cl$	~0.025[i]
$-CF_3$	0.077
=O	8.9
-CHO O ‖ -C-	0.76[j]
O ‖ $-CH_2C-$	4.6
O ‖ -CHC- O ‖ →CC-	4.6[k]
$-C_6H_5$	~1.0[l]
-OH	3.5
-O-	7.0
O ‖ -C-OR	~0.0
O ‖ -OCR	1.4
$-CH_2ONO_2$ $>CHONO_2$ $->CONO_2$	0.45[m]

(continued)

Table 15 (continued) - 3

Substituent Group, X	Factor F(X)
$-ONO_2$	0.024
$-C=C<$ $-C\equiv C-$	$\lesssim 1$[n]
$-CN$	0.14[o]
Three-membered ring	0.017
Four-membered ring	0.22
Five-membered ring	0.80
Six-membered ring	1.00
Seven-membered ring	~1.0

[a] Derived from the product analysis data for CH_3OH (see Atkinson 1985).
[b] By definition (see text).
[c] A non-linear least squares fit, with $F(-CH_2-) \neq F(>CH-) \neq F(>C<)$ yielded similar values of these group factors, with no trend along the group. The factor given arises from assuming that $F(-CH_2-) = F(>CH-) = F(>C<)$.
[d] Derived from the recommended rate constant for CH_3Br.
[e] Because of lack of data, $F(-CH_2Cl)$, $F(-CHCl_2)$ and $F(-CH_2Br)$ are assumed to be equal.
[f] Derived from the recommended rate constant for CH_3CCl_3.
[g] Derived from the available rate constants for CH_3CH_2F and CH_2FCH_2F.
[h] Derived from the available rate constants for CH_3CHF_2 and CH_2FCHF_2.
[i] Derived from the recommended rate constant of Atkinson (1985) for CH_3CF_2Cl.
[j] $F(-CHO)$ assumed to be identical to $F(-\overset{O}{\overset{\|}{C}}-)$.
[k] Assumed to be identical to that for $-CH_2\overset{O}{\overset{\|}{C}}-$.
[l] Approximate value to fit the abstraction rate constants derived by Atkinson (1985).
[m] Because of lack of wide data base, assumed equal.
[n] Based upon observation of negligible H-atom abstraction from allylic C-H bonds (see text).
[o] Derived from recommendation of Atkinson (1985) for acetonitrile (CH_3CN).

Table 16. Comparison of Experimental and Calculated Room Temperature Rate Constants for the Reactions of OH Radicals with a Series of Organic Compounds which Proceed via Overall H-Atom Abstraction (Underlined Rate Constants are Those Used in Derivation of the Group Rate Constants and Factors Given in Table 15)

Organic	$10^{12} \times k_{total}$ (cm^3 $molecule^{-1}$ s^{-1})	
	Calculated	Experimental
Alkanes		
Ethane	0.286	0.275
Propane	1.19	1.15
n-Butane	2.51	2.53
2-Methylpropane	2.37	2.37
n-Pentane	3.89	4.0
2-Methylbutane	3.98	3.9
2,2-Dimethylpropane	0.744	0.868
n-Hexane	5.28	5.58
2-Methylpentane	5.37	5.5
3-Methylpentane	5.75	5.6
2,2-Dimethylbutane	1.81	2.6
2,3-Dimethylbutane	5.45	6.2
n-Heptane	6.67	7.2
2,4-Dimethylpentane	6.84	5.1
2,2,3-Trimethylbutane	3.28	4.1
n-Octane	8.06	8.72
2,2,4-Trimethylpentane	4.67	3.66
2,2,3,3-Tetramethylbutane	1.12	1.06
n-Nonane	9.44	10.0
n-Decane	10.8	11.2
n-Undecane	12.2	13.3
n-Didecane	13.6	13.9
n-Tridecane	15.0	15.5
Cyclopropane	0.07	0.07
Cyclobutane	1.2	1.2

(continued)

Table 16 (continued) - 2

Organic	$10^{12} \times k_{total}$ (cm^3 $molecule^{-1}$ s^{-1}) Calculated	Experimental
Cyclopentane	5.5	5.2
Cyclohexane	8.32	7.38
1-Methylcyclohexane	10.2	10.3
Cycloheptane	9.7	13.1
Bicyclo[2.2.1]heptane	9.5	5.42
Bicyclo[2.2.2]octane	16	14.5
Bicyclo[3.3.0]octane	10	10.9
cis-Bicyclo[4.3.0]nonane	14	17.0
trans-Bicyclo[4.3.0]nonane	14	17.4
cis-Bicyclo[4.4.0]decane	19.1	19.6
trans-Bicyclo[4.4.0]decane	19.1	20.2
Tricyclo[$5.2.1.0^{2,6}$]decane	12	11.2
Tricyclo[$3.3.1.1^{3,7}$]decane	22.4	22.7
Haloalkanes		
CH_3F	0.014	0.0168
CH_3Cl	0.054	0.0436
CH_3Br	0.043	0.0393
CH_2F_2	0.0081	0.0109
CH_2FCl	0.031	0.0441
CH_2Cl_2	0.12	0.142
CHF_3	0.0018	0.00020
CHF_2Cl	0.0067	0.00468
$CHFCl_2$	0.026	0.0303
$CHCl_3$	0.099	0.103
CH_3CH_2F	0.20[a]	0.23
CH_3CH_2Cl	0.39	0.40
CH_3CHF_2	0.032	0.034
CH_2FCH_2F	0.14	0.11
CH_3CHCl_2	0.34	0.26

(continued)

Table 16 (continued) - 3

Organic	$10^{12} \times k_{total}$ (cm^3 $molecule^{-1}$ s^{-1}) Calculated	Experimental
CH_2ClCH_2Cl	0.36	0.22
CH_2BrCH_2Br	0.29	0.25
CH_3CF_3	0.011	~0.002
CH_2FCHF_2	0.023	0.018
CH_3CF_2Cl	0.0036	0.00358
CH_3CCl_3	0.012	0.0119
$CH_2ClCHCl_2$	0.33	0.328
CH_2FCF_3	0.0063	0.00854
CH_2ClCF_3	0.024	0.0162
CH_2ClCF_2Cl	0.0078	$\leq$0.019
CHF_2CF_3	0.0014	0.0025
$CHFClCF_3$	0.0052	0.0102
$CHCl_2CF_3$	0.020	0.0335
Aldehydes		
Formaldehyde	7.3	9.0
Acetaldehyde	16	16.2
1-Propanal	22	19.6
1-Butanal	26	23
2-Methyl-1-propanal	24	27
1-Pentanal	28	27
3-Methyl-1-butanal	30	27
2,2-Dimethyl-1-propanal	23	27
Benzaldehyde	16	13.0
Ketones		
Acetone	0.22	0.23
2-Butanone	1.34	1.0
2-Pentanone	4.8	4.64
3-Pentanone	2.5	1.82

(continued)

Table 16 (continued) - 4

Organic	$10^{12} \times k_{total}$ (cm^3 $molecule^{-1}$ s^{-1}) Calculated	Experimental
2-Hexanone	7.0	8.97
3-Hexanone	6.0	6.81
2,4-Dimethyl-3-pentanone	5.3	5.31
4-Methyl-2-pentanone	9.5	14.1
2,6-Dimethyl-4-heptanone	19	27.1
α-Dicarbonyls		
Glyoxal	24	11.2
Methylglyoxal	12	16.9
Biacetyl	0.22	0.24
Alcohols		
Methanol	0.63	0.9
Ethanol	3.2	2.9
1-Propanol	5.1	5.3
2-Propanol	6.8	6.2
1-Butanol	6.5	7.3
2-Methyl-2-propanol	0.69	1.09
Glycols		
1,2-Ethanediol	7.7	7.7
1,2-Propanediol	12	12
Dihydroxyethylether	23	30
2-Chloroethanol	4.3	1.4
Ethers		
Dimethyl ether	2.0	3.51
Diethyl ether	12	9.2
Di-n-propyl ether	18	16.8
Methyl-t-butyl ether	1.6	2.64

(continued)

Table 16 (continued) - 5

Organic	$10^{12} \times k_{total}$ (cm^3 $molecule^{-1}$ s^{-1}) Calculated	Experimental
Tetrahydrofuran	14	15
Ethene oxide	0.25	0.07
Propene oxide	0.41	0.52
1,2-Butene oxide	0.51	2.1
1-Chloro-2,3-epoxypropane	0.50	0.44
Esters		
Methyl acetate	0.19	0.17
Ethyl acetate	1.3	1.82
n-Propyl acetate	2.7	4.2
sec-Butyl acetate	4.2	5.4
Methyl propionate	0.38	0.27
Ethyl propionate	1.5	1.66
Nitrates		
2-Propyl nitrate	0.17	0.18
1-Butyl nitrate	1.8	1.39
2-Butyl nitrate	0.68	0.67
2-Pentyl nitrate	1.9	1.83
3-Pentyl nitrate	1.2	1.10
3-Methyl-3-butyl nitrate	1.3	1.72
2,2-Dimethyl-1-propyl nitrate	0.58	0.85
2-Hexyl nitrate	3.3	3.13
3-Hexyl nitrate	2.4	2.66
Cyclohexyl nitrate	5.2	3.29
2-Methyl-2-pentyl nitrate	0.69	1.71
3-Methyl-2-pentyl nitrate	2.4	3.01
3-Heptyl nitrate	3.8	3.64
3-Octyl nitrate	5.2	3.82

(continued)

Table 16 (continued) - 6

Organic	$10^{12} \times k_{total}$ (cm^3 $molecule^{-1}$ s^{-1}) Calculated	Experimental
Nitriles		
CH_3CN	0.02	0.02
CH_3CH_2CN	0.30	0.19

[a]While this overall rate constant agrees well with that experimentally observed value, the calculated distribution of H-atom abstraction from the α- and β-carbon atoms do not. Thus we calculate only ~41% H-atom abstraction from the α-carbon, compared with the experimentally observed percentage of 85 ± 3% (Singleton et al. 1980).

Similarly, the rate constants for the ethers, esters, alcohols, carboxylic acids, nitrates and nitriles are used to derive the factors F(-O-), F(-OC(=O)-), F(-C(=O)O-), F(-OH), F(-ONO_2), F(-CH_2ONO_2), F(>$CHONO_2$), F(>$CONO_2$) and F(-CN) given in Table 15. The calculated rate constants at ~298 K using these factors for a series of organics are compared with the experimental values in Table 16, and good agreement, typically to within a factor of ~2, is seen.

Alkenes, Alkynes and Aromatics. The observations that at room temperature H-atom abstraction from propene and 1-butene are negligible (<2% and <10%, respectively) allow upper limit values of F(>C=C<) to be derived. Since H-atom abstraction from C-H bonds in the >CH-C≡C- structural unit is expected to be less important than from C-H bonds in >CH-C=C<, we use this latter value for abstraction from the >CH-C≡C- unit also. Similarly, for the aromatic hydrocarbons, the rate constants for H-atom abstraction from the substituent -CH_3 groups allow the factor F(-C_6H_5) to be derived.

Effects of Ring Strain. Atkinson et al. (1983a) and Jolly et al. (1985) have shown that in the cycloalkanes the presence of a ring strain energy of ≥5 kcal $mole^{-1}$ leads to a decrease of the experimental rate constants, compared to those predicted in the absence of ring strain. This is primarily due to the fact that the C-H bond dissociation energies

in these strained cycloalkanes are significantly higher than those in the acyclic alkanes (McMillen and Golden 1982), and hence a knowledge of the precise bond dissociation energies in these cycloalkanes again allows the H-atom abstraction rate constants to be reliably estimated (Jolly et al. 1985). However, such data are available for only a small number of cycloalkanes, and for a-priori predictive purposes a more parametric approach is necessary.

Atkinson et al. (1983a) have shown that a total ring strain energy in excess of ~5 kcal $mole^{-1}$ leads to a decrease in the observed room temperature rate constants for a series of bi- and tricycloalkanes, over those predicted in the absence of ring strain, with k_{obs}/k_{calc} decreasing approximately exponentially with increasing ring strain energies. Since for polycyclic systems the overall ring strain energies are approximately the sum of the ring strain energies per ring (Benson 1976), a correction factor per ring can be derived. For polycyclic systems these correction factors, F_{ring}, are then multiplicative. For example, for bicyclo[4.3.0]-nonane the rate constant is given by

$$k_{total} = 3\ k^{o}_{sec}\ [F(-CH_2-)]^2 + 4\ k^{o}_{sec}\ F(-CH_2-)\ F(>CH-)$$

$$+ 2\ k^{o}_{tert}\ [F(-CH_2-)]^2\ F(>CH-)\ \ F_5\ F_6$$

where F_6 and F_5 are the correction factors for six-membered and five-membered rings, respectively. From an analysis of the room temperature rate constants for the C_3-C_7 cycloalkanes, and the bi- and tricycloalkanes studied by Atkinson et al. (1983a), the ring correction factors given in Table 15 are derived. These ring strain correction factors then allow the estimation of H-atom abstraction rate constants for strained ring systems.

Furthermore, since the ring strain energies for ring systems containing O-, N- and S-heteroatoms are similar to the corresponding cycloalkane rings (Benson 1976), they can be used for the estimation of H-atom abstraction rate constants for heteroatom-containing rings, such as the oxides and cycloethers.

A comparison of the experimentally observed and calculated room temperature rate constants are given in Table 16 for the OH radical reactions which proceed via H-atom abstraction. Of the 128 organics listed, only for six do the experimental and calculated rate constants disagree by more than a factor of 2.

There are only a limited number of organics (all alkanes) for which OD radical rate constants are available and which proceed via H-atom abstraction. From these data, assuming that deuterium isotope substitution leads to a constant decrease in the abstraction rate constant per $-CD_3$, $-CD_2-$ and >CD- group, relative to the corresponding $-CH_3$, $-CH_2$ and >CH- groups, this factor is 0.28 at room temperature. Thus (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}), at room temperature $k^o_{primary}$ $(-CD_3)$ = 0.04; $k^o_{secondary}$ $(-CD_2-)$ = 0.23 and $k^o_{tertiary}$ (>CH-) = 0.51, with $F(-CD_2-)$ = F(>CD-) = 1.30 being set equal to the corresponding factors for $F(-CH_2-)$ = F(>CH-). These group rate constants fit the room temperature rate constants of Paraskevopoulos and Nip (1980) and Tully et al. (1985) for n-C_4D_{10}, $(CD_3)_3CH$, $(CH_3)_3CD$, $(CD_3)_3CD$ and $(CD_3)_4C$ to within ~30%.

OH Radical Addition to Unsaturated >C=C< and -C≡C- Bonds

Alkenes and Alkynes. The a-priori prediction of room temperature OH radical reaction rate constants involving OH radical addition to alkenes has been discussed recently by Ohta (1983, 1984), and Atkinson et al. (1983d) and Atkinson and Aschmann (1984b). The approach used by these authors is analogous to that presented earlier by Hendry and Kenley (1979), and is based upon the number of unconjugated double bonds or conjugated double bond systems and the degree, identity and configuration of substitution around these double bonds. As an example, 2-methyl-1,4-pentadiene ($CH_2=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_2-CH=CH_2$) contains a 1,1-dialkylsubstituted double bond ($CH_2=C<$) plus a mono alkyl-substituted double bond ($CH_2=CH-$) and the overall rate constant is given by the sum of the rate constants for 2-methylpropene (for $CH_2=C<$) and propene (for $CH_2=CH-$) [Atkinson et al. 1983d].

For the conjugated dialkenes the approaches used by Ohta (1983, 1984) and Atkinson et al. (1983d) differ somewhat, but yield similar results for the data set presently available. Atkinson et al. (1983d) consider the >C=C-C=C< moiety as a single unit with the rate constant depending solely

on the number of alkyl substituents around this structural unit. Thus, for example, for 2-methyl-6-methylene-2,7-octadiene [$(CH_3)_2C{=}CH_2CH_2CH_2\underset{\displaystyle CH_2}{\overset{\displaystyle |}{C}}CH$ = CH_2] the overall OH radical addition rate constant is given by the sum of the rate constants for 2-methylpropene ($CH_2{=}C<$) and the $CH_2{=}CH{-}\underset{\displaystyle |}{C}{=}CH_2$ entity. Ohta (1983, 1984) rather considers this conjugated $>C{=}\underset{\displaystyle |}{C}{-}\underset{\displaystyle |}{C}{=}C<$ unit as being comprised of the individual $>C{=}\underset{\displaystyle |}{C}-$ and $-\underset{\displaystyle |}{C}{=}C<$ monoalkene units, with the rate constants for the corresponding monoalkene units multiplied by a factor of 1.24 (Ohta 1983). Thus, for example, the rate constant for 2-methyl-1,3-butadiene [$CH_2{=}CHC(CH_3){=}CH_2$] is derived from that for the $CH_2{=}CH-$ unit (propene) plus that for $CH_2{=}C<$ (isobutene), multiplied by 1.24.

Both approaches yield similar results (see Table 17) and both are equally applicable. Only when kinetic data become available for non-alkyl substituted $>C{=}\underset{\displaystyle |}{C}{-}\underset{\displaystyle |}{C}{=}C<$ systems will it become evident which of these two approaches to the a-priori prediction of addition rate constants for conjugated dialkane systems is superior.

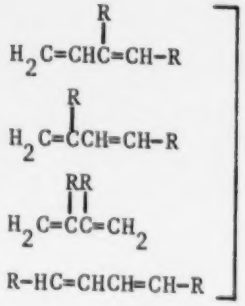
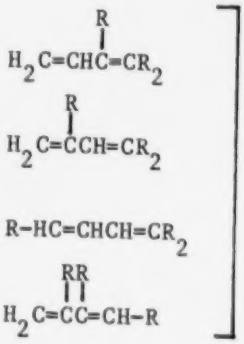
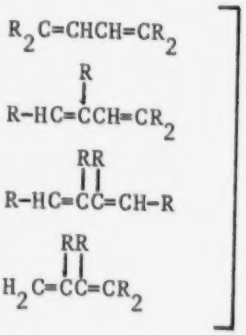
The group rate constants, their derivations and a comparison of predicted and experimental room temperature rate constants for the acyclic and cyclic monoalkenes and conjugated dialkenes are given in Table 17. For the dialkenes and cyclodialkenes containing nonconjugated $>C{=}C<$ bonds and for other alkenes and cycloalkenes containing both $>C{=}C<$ and $>C{=}\underset{\displaystyle |}{C}{-}\underset{\displaystyle |}{C}{=}C<$ units, calculated and experimental data are given in Table 18. These experimental data utilized include those derived directly, together with the rate constants derived from the NO_x-photooxidation rates of Grimsrud et al. (1975) at 301 ± 1 K. These latter data must be viewed as semi-quantitative only, since their use assumes that the OH radical concentrations were identical in the separate-NO_x-organic-air irradiations and that O_3 reactions were negligible. The agreement between the calculated and experimental room temperature rate constants is seen to be generally excellent. Furthermore, for the alkenes containing $>C{=}\underset{\displaystyle |}{C}{-}\underset{\displaystyle |}{C}{=}C<$ structural units, the use of the techniques advanced by Ohta (1983, 1984) and Atkinson et al. (1983d) yield very similar predicted rate constants. The use of either is recommended.

Table 17. Comparison of Room Temperature Recommended, Experimentally Observed and Calculated Rate Constants for the Addition of OH Radicals to Monoalkenes, Conjugated Dialkenes and Alkynes with Varying Degrees and Configuration of Alkyl Substitution and Factors for Nonalkyl Substituents

General Structure	10^{11} x k [recommended] (cm^3 $molecule^{-1}$ s^{-1})	Alkene or Alkyne	10^{11} x k [observed] (cm^3 $molecule^{-1}$ s^{-1})
$CH_2=CH-R$	2.63[a]	Propene	2.63
		1-Butene	3.14
		1-Pentene	3.14
		3-Methyl-1-butene	3.18
		1-Hexene	3.7
		3,3-Dimethyl-1-butene	2.84
		1-Heptene	4.0
$CH_2=C(R)(R)$	5.14[b]	2-Methylpropene	5.14
		2-Methyl-2-butene	6.07
		2-Methyl-1-pentene	6.26
		β-Pinene	7.85
cis-R-CH=CH-R	5.61[c]	cis-2-Butene	5.61
		cis-2-Pentene	6.51
		Cyclopentene	6.70
		Cyclohexene	6.74
		Cycloheptene	7.41
		Bicyclo[2.2.1]-2-heptene	4.91
		Bicyclo[2.2.2]-2-octene	4.06
trans-R-CH=CH-R	6.37[d]	trans-2-Butene	6.37
		trans-2-Pentene	6.7
		trans-4-Methyl-2-pentene	6.08
		trans-4,4-Dimethyl-2-pentene	5.48
$R-CH=C(R)(R)$	8.69[e]	2-Methyl-2-butene	8.69
		2-Methyl-2-pentene	8.88
		α-Pinene	6.12
		1-Methylcyclohexene	9.5
$R_2C=CR_2$	10.7[f]	2,3-Dimethyl-2-butene	10.7
		2,3-Dimethyl-2-pentene	10.2
$H_2C=CHCH=CH-R$ / $H_2C=CHC(R)=CH_2$	10.5[g]	cis-1,3-Pentadiene	10.1 (10.2)[h]
		2-Methyl-1,3-butadiene	10.1 (9.6)
		trans-1,3-Hexadiene	11.3 (10.2)

(continued)

Table 17 (continued) - 2

General Structure	10^{11} x k [recommended] (cm^3 $molecule^{-1}$ s^{-1})	Alkene or Alkyne	10^{11} x k [observed] (cm^3 $molecule^{-1}$ s^{-1})
	13.8[g]	cis-, trans-2,4-hexadiene	13.5 (14.9)
		2-Methyl-1,3-pentadiene	13.7(~13.8)
		4-Methyl-1,3-pentadiene	13.7 (14.0)
		2,3-Dimethyl-1,3-butadiene	12.2 (12.7)
		1,3-Cyclohexadiene	16.3 (13.9)
		1,3-Cycloheptadiene	13.9 (13.9)
	~18.0[i]		(14.0)
			(17.1)
			(~18.2)
			(17.1)
	21.1[g]		(21.6)
			(21.6)
		2,5-Dimethyl-2,4-hexadiene	21.1 (21.6)
			(19.6)
$H_2C=C=CH-R$	3.1[g]	1,2-Butadiene	2.6
		1,2-Pentadiene	3.56

(continued)

Table 17 (continued) - 3

General Structure	10^{11} x k [recommended] (cm^3 $molecule^{-1}$ s^{-1})	Alkene or Alkyne	10^{11} x k [observed] (cm^3 $molecule^{-1}$ s^{-1})
$H_2C{=}C{=}C(R)(R)$	5.7[g]	3-Methyl-1,2-butadiene	5.71
HC≡C-R	0.7[g]	Propyne	0.61
		1-Butyne	0.80

Group	Factor C
-F, -Cl, -Br	0.25[j]
$-CH_2Cl$	0.8[k]
-CN	0.15[l]
-CHO	~0.2[m]
$-COCH_3$	0.9[n]
$-OCH_3$	1.3[o]

[a]Derived from propene.
[b]Derived from 2-methylpropene.
[c]Derived from cis-2-butene.
[d]Derived from trans-2-butene.
[e]Derived from 2-methyl-2-butene.
[f]Derived from 2,3-dimethyl-2-butene.
[g]Derived from the dialkenes or alkynes shown.
[h]Rate constants in parentheses are those calculated by the technique described by Ohta (1983, 1984) [see text].
[i]No experimental data available; derived by using a factor of 1.4 per alkyl substituent on 1,3-butadiene based upon the recommendations of Atkinson (1985) for the one, two and four alkyl-substituted >C=C-C=C< entities.
[j]Derived from the rate constants for CH_2=CHF, CH_2=CHCl, CH_2=CHBr, CH_2CF_2, CHCl=CCl_2, CCl_2=CCl_2 and CFCl=CF_2.
[k]Derived from fitting experimental and calculated rate constants for cis- and trans-1,3-dichloropropene and 2-chloromethyl-3-chloro-1-propene.
[l]Derived from the rate constant for CH_3CN.
[m]Derived from the rate constants for CH_2=CHCHO, CH_3CH=CHCHO and CH_2=$C(CH_3)$CHO.
[n]Derived from the rate constants for CH_2=$CHCOCH_3$ and cis- and trans-3-hexene-2,5-dione.
[o]Derived from the rate constant for CH_2=$CHOCH_3$.

Table 18. Comparison of Experimental and Calculated Room Temperature Rate Constants for Alkenes Containing Multiple >C=C< or >C=C-C=C< Structural Units, and for Heteroatom-Containing Alkenes

Alkene or Substituted Alkene	$10^{11} \times k$ (cm^3 $molecule^{-1}$ s^{-1}) Calculated	Observed
1,4-Pentadiene	5.26	5.33
trans-1,4-Hexadiene	9.00	9.1
1,5-Hexadiene	5.26	6.2
2-Methyl-1,4-pentadiene	7.77	7.9
2-Methyl-1,5-hexadiene	7.77	9.6
2,5-Dimethyl-1,5-hexadiene	10.3	12.0
1,4-Cyclohexadiene	11.2	9.9
Bicyclo[2.2.1]-2,5-heptadiene	11.2	12.0
d-Limonene	14.6	13.8
3,7-Dimethyl-1,6-octadiene	11.3	18[a]
3-Methylene-7-methyl-1,6-octadiene	19.2	23[a]
cis-3,7-Dimethyl-1,3,6-octatriene	22.5 (22.7)[b]	32[a]
Δ^3-Carene	8.69	8.4[a]
β-Phellandrene	13.8 (13.3)[b]	11[a]
Carvomethene	8.69	13[a]
Terpinolene	19.4	66[a,c]
α-Phellandrene	18 (17.7)[b]	72[a,c]
α-Terpinene	21.1 (21.6)[b]	330-660[a,c]
Vinyl fluoride	0.66	0.556
Vinyl chloride	0.66	0.660
Vinyl bromide	0.66	0.681
1,1-Difluoroethene	0.32	0.2-0.25
Trichloroethene	0.14	0.24
Tetrachloroethene	0.042	0.017
Chlorotrifluoroethene	0.042	~0.7
cis-1,3-Dichloropropene	1.1	0.75
trans-1,3-Dichloropropene	1.3	1.26
2-Chloromethyl-3-chloro-1-propene	3.3	4.0

(continued)

Table 18 (continued) - 2

Alkene or Substituted Alkene	10^{11} x k (cm^3 $molecule^{-1}$ s^{-1}) Calculated	Observed
Methyl vinyl ketone	2.4	1.85
cis-3-hexene-2,5-dione	4.5	6.3
trans-3-hexene-2,5-dione	5.2	5.3
Acrylonitrile (CH_2=CHCN)	0.39	~0.4
Vinyl methyl ether	3.4	3.35

[a]Derived from the NO_x-photooxidation study of Grimsrud et al. (1975) [see text].
[b]Calculated using the technique of Ohta (1983, 1984) [see text].
[c]Probably high due to contribution from O_3 reaction.

For use at temperatures other than room temperature, a temperature dependence equivalent to an Arrhenius activation energy of -1.0 kcal $mole^{-1}$ should be used.

Insufficient data exist for reliable a-priori predictions for the 1,2-dialkenes and the alkynes, since only the group rate constants CH_2=C=CH-, CH_2=C=C< and HC≡C- can be derived from the rate constants presently available. These group rate constants are included in Table 17 and are used for comparison with the experimental data in Table 17. We do not deal with the conjugated trialkenes, due to insufficient data (though the general technique of Ohta (1983) may be applicable to this class of alkenes).

Haloalkenes and Oxygen-Containing Organics with Unsaturated >C=C< Bonds. In order to predict the rate constants for the haloalkenes and for various classes of oxygenates containing >C=C< double bonds, we employ factors to account for the bonding of halogen and oxygen atoms and of carbonyl groups to the >C=C< double bond. The use of these factors is illustrated as follows: the rate constant for vinyl chloride (CH_2=CHCl) is that for CH_2=CH- (i.e., propene) multiplied by the factor C(Cl); that

for trichloroethene ($CHCl=CCl_2$) is that for -CH=C< (i.e., 2-methyl-2-butene) x $C(Cl)^3$.

The factors derived from the fairly limited data set available [the haloalkenes, including those studied by Howard (1976), $CH_2=CHOCH_3$, $CH_2=CHCOCH_3$, $CH_2=CHCN$, cis- and trans-1,3,-dichloropropene, $CH_2=C(CH_2Cl)_2$, cis- and trans-$CH_3COCH=CHCOCH_3$ (the α,β-unsaturated aldehydes such as $CH_2=CHCHO$ cannot be used directly due to the concurrent reaction pathway involving H-atom abstraction from the -CHO group)] are given in Table 17. A comparison of calculated and experimentally determined rate constants are given in Table 18. It should be noted that since most of the available data have been utilized in deriving these factors, the observed reasonable agreement may be fortuitous. For the -CHO group we have estimated an approximate factor which yields OH radical addition (and hence by difference the H-atom abstraction) rate constants for $CH_2=CHCHO$, $CH_3CH=CHCHO$ and $CH_2C(CH_3)CHO$ consistent with our discussion above dealing with these α,β-unsaturated aldehydes.

(3) OH Radical Addition to Aromatic Rings. Based upon the literature data, the optimum approach to the a-priori prediction of room temperature rate constants for OH radical addition to the aromatic ring appears to be that of Zetzsch (1982). This a-priori predictive technique utilizes the excellent correlation (Zetzsch 1982, Atkinson et al. 1985a) between the OH radical rate constants k^{add} for addition to the aromatic ring and the sum of the electrophilic substituent constants, $\Sigma\sigma^+$, of Brown and Okamoto (1958). Thus Zetzsch (1982) reported that for benzene, a series of substituted monocyclic aromatics (excluding benzaldehyde since H-atom abstraction is the major reaction pathway for this aromatic) and biphenyl

$$\log k^{add} \ (cm^3 \ molecule^{-1} \ s^{-1}) = -11.4 \pm 1.39 \ \Sigma\sigma^+.$$

In Table 19 we have listed the available room temperature rate constants for the addition of OH radicals to benzene, substituted monocyclic aromatics and biphenyl (using our recommendations where possible). We have omitted benzaldehyde (since H-atom abstraction is the major reaction route for this compound), and aniline, p-chloroaniline and n-propylpentafluorobenzene from this list, since significant and presently

Table 19. Comparison of Experimentally Observed and Calculated Room Temperature Rate Constants for the Addition of OH Radicals to Benzene, Biphenyl and a Series of Substituted Monocyclic Aromatics

Aromatic	$\Sigma\sigma^+$	$10^{12} \times k_{addition}$ (cm^3 $molecule^{-1}$ s^{-1})	
		Observed[a]	Calculated
Benzene	0	1.19	2.3
Toluene	-0.311	5.7	6.2
o-Xylene	-0.377	13.4	7.6
m-Xylene	-0.622	23.5	16.5
p-Xylene	-0.377	14.1	7.6
1,2,3-Trimethylbenzene	-0.688	31.6	20.4
1,2,4-Trimethylbenzene	-0.688	38.4	20.4
1,3,5-Trimethylbenzene	-0.933	60.5	44.2
Ethylbenzene	-0.295	7.5	5.9
n-Propylbenzene	-0.295	5.7	5.9
Isopropylbenzene	-0.280	6.6	5.6
Phenol	-0.92	28.3	42.5
Methoxybenzene	-0.778	15.7	27.1
o-Cresol	-0.986	37	52.3
m-Cresol	-1.231	54	114
p-Cresol	-0.986	41	52.3
o-Ethyltoluene	-0.375	12.0	7.6
m-Ethyltoluene	-0.606	17.1	15.7
p-Ethyltoluene	-0.375	11.4	7.6
Fluorobenzene[b]	-0.073	0.54	2.9
Chlorobenzene	0.114	0.94	1.6
Bromobenzene[b]	0.150	0.70	1.4
Iodobenzene[b]	0.135	0.93	1.5
Benzotrifluoride	0.520	0.48	0.44
Aniline[b]	-1.3	119	142
Benzonitrile	0.562	0.33	0.39
Nitrobenzene	0.674	0.21	0.27
4-Chlorobenzotrifluoride	0.634	0.25	0.31
o-Dichlorobenzene	0.513	0.42	0.45
m-Dichlorobenzene	0.228	0.72	1.12
p-Dichlorobenzene	0.513	0.32	0.45
p-Chloroaniline[b]	-0.901	83.0	40.0
o-Nitrophenol[b]	-0.13	0.90	3.5
1,2,4-Trichlorobenzene	0.627	0.532	0.32
n-Propylpentafluorobenzene[b]	0.419	3.06	0.61
Hexafluorobenzene	0.837	0.219	0.16
Biphenyl (per ring)	-0.179	3.5	4.1

[a]Account has been taken wherever possible, for the H-atom abstraction pathway.

[b]Not used in deriving the correlation (see text).

unknown, amounts of the OH radical reactions with these substituted aromatics may proceed via H-atom abstraction from the substituent groups. Furthermore, because of the limited information available, we have also not included the reported data for fluorobenzene, bromobenzene, iodobenzene and o-nitrophenol in our derivation of the best-fit correlation. The observed overall OH radical reaction rate constants for the contribution due to the H-atom abstraction pathway have been corrected, wherever possible (see Atkinson 1985). Additionally, our recommended rate constant for biphenyl has been divided by a factor of two to take into account the two identical aromatic rings to which OH radical addition can take place.

The values of $\Sigma\sigma^+$ listed in Table 19 were calculated as described by Zetzsch (1982), i.e., (a) steric hindrance was neglected, and the electrophilic substituent constant of the ortho position was set equal to that for the para position; (b) the total substituent constant $\Sigma\sigma^+$ was the sum of all substituent constants of the substituents connected to the aromatic ring; (c) the OH radical adds to the position yielding the most negative value for $\Sigma\sigma^+$ (preferably a free position); and (d) if all positions are occupied, the ipso-position was treated as a meta-position.

A unit-weighted least-squares analysis of these values of k^{add} and $\Sigma\sigma^+$ yields the expression

$$\log k^{add} \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = -11.64 - 1.38\ \Sigma\sigma^+,$$

which is only slightly different from that given by Zetzsch (1982).

The OH radical addition rate constants at room temperature calculated from this equation are compared to the experimental values in Table 19 and Figure 6, and it can be seen that only for m-cresol, fluorobenzene and o-nitrophenol are the discrepancies between the measured and calculated values of k^{add} greater than a factor of 2. For the other 34 aromatics given in Table 19, the estimated values of k^{add} are within a factor of 2 of the measured rate constants, even though the absolute magnitude of these measured rate constants vary by a factor of ~300.

Clearly, this correlation can be used to a-priori predict the room temperature rate constants for the addition of OH radicals to the aromatic ring to within ± a factor of typically $\lesssim$2. As an example of interest,

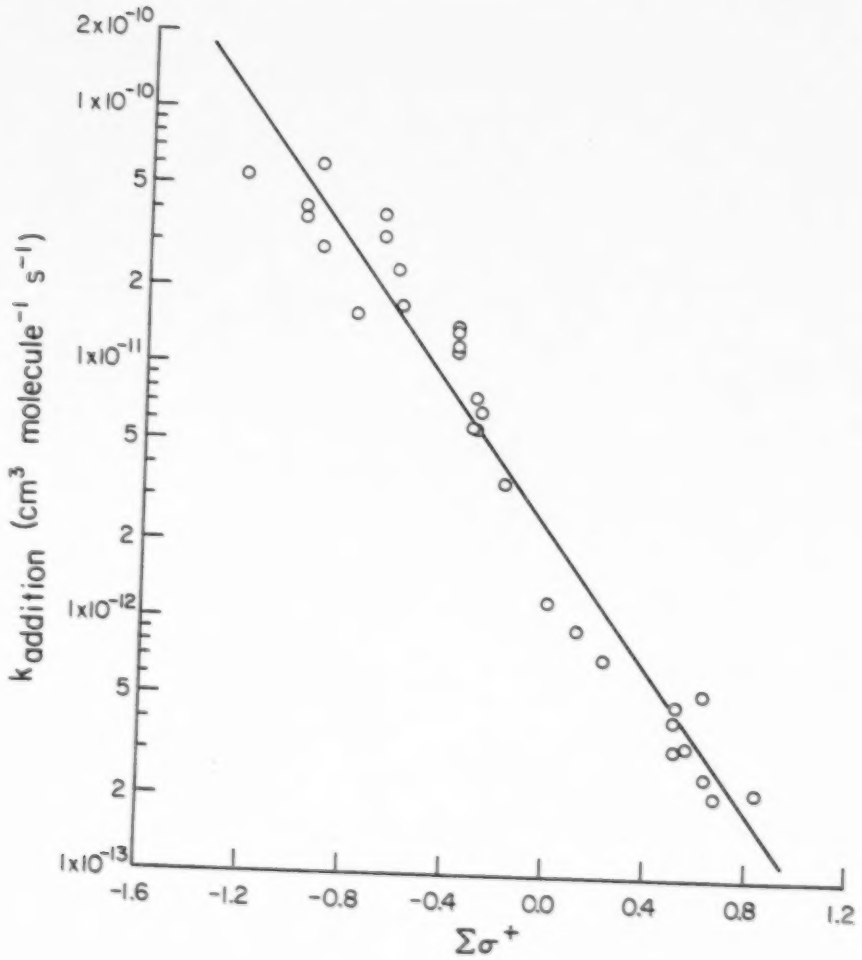


Figure 6. Plot of log $k_{addition}$ against the overall electrophilic substituent constants for a series of aromatic compounds (see text).

this correlation predicts room temperature rate constants for OH radical addition to aniline and p-chloroaniline of 1.4×10^{-10} cm^3 $molecule^{-1}$ s^{-1} and 4.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively, which can be compared to the measured rate constants of 1.2×10^{-10} cm^3 $molecule^{-1}$ s^{-1} and 8.3×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively. This suggests, perhaps surprisingly in view of the high reactivity of the aliphatic amines, that the OH radical addition process is dominant for aniline and significant for p-chloroaniline.

The use of the above a-priori predictive techniques, namely those applicable to H-atom abstraction from C-H (and, to a lesser extent from O-H) bonds, and OH radical addition to double and triple carbon-carbon bonds and to aromatic rings, enable OH radical reaction rate constants to be estimated with apparently reasonable reliability. It should, however, be noted that the available kinetic data base for sulfur-, nitrogen- and phosphorous-containing organics, and for organometallics, is presently insufficient for the extension of our predictive techniques to these important classes of organics. Hopefully, this deficiency will be reduced with the development of the necessary data base in future years. However, the present predictive technique appears to be able to predict, solely from the chemical structure of the organic compound, room temperature rate constants to within a factor of <5 (and often to within a factor of 2 or better) for a number of classes of organic compounds.

Conclusions

In the above sections we have extended previous a-priori predictive schemes to develop an up-to-date estimation procedure which will hopefully prove useful for room temperature rate constant and atmospheric lifetime calculations.

5. ATMOSPHERIC LIFETIMES

The lifetimes of organic chemicals with respect to reaction with the OH radical, τ_{OH}, the NO_3 radical, τ_{NO_3}, and with O_3, τ_{O_3}, can be determined from a knowledge of the relevant reaction rate constants k^{OH}, k^{NO_3} and k^{O_3} and the atmospheric OH radical, NO_3 radical and O_3 concentrations, from the equation

$$\tau_X = (k^X [X])^{-1}$$

where X = OH, NO_3, and O_3. However, in general this equation only yields the instantaneous lifetime, since the OH radical, NO_3 radical and O_3 concentrations exhibit seasonal, altitudinal, diurnal and geographical variations, and the rate constants typically vary with temperature, which decreases with increasing altitude in the troposphere.

Variations in k^{OH} due to pressure are expected to be minor, except possibly for HCN, since most organic compounds studied to date are in the limiting high pressure second-order kinetic regime at total pressures of ~200 torr of air or lower.

Chang and Kaufman (1977) and Altshuller (1980) have discussed the derivation of atmospheric lifetimes for reaction with the OH radical for a series of organics. As discussed, differing assumptions of tropospheric OH radical concentration profiles as a function of altitude affect the resulting calculated lifetimes. Altshuller (1980) used a weighted average tropospheric temperature of 265 K to calculate lifetimes due to reaction with OH radicals and an average OH radical concentration derived from tropospheric halocarbon measurements. While this use of an average tropospheric temperature of 265 K is reasonably appropriate for the alkanes and other organics which exhibit positive temperature dependencies, its use may lead to discrepancies for these organics whose temperature dependence is negative (an obvious example being tetrachloroethene). Similar considerations apply to the O_3 and NO_3 radical reactions.

Based upon the recent modeling study of Crutzen (1982), seasonally and diurnally averaged tropospheric northern and southern hemispheric OH radical concentrations are ~5 x 10^5 molecule cm^{-3} and ~6 x 10^5 molecule cm^{-3}, respectively. These estimates are in good agreement with previous

estimates based upon, for example, the observed concentrations of $CHCl_3$ and CH_3Cl_3 and of ^{14}CO, and can be used to derive the lifetimes due to OH radical reaction of organics which are well-mixed throughout the troposphere. For organics which have lifetimes short with respect to the tropospheric mixing time, for example of the order of a few days or less, the use of averaged temperatures and OH radical concentrations will lead to errors. However, since the actual instantaneous OH radical concentrations are not known to within at least a factor of 2, such errors may not be significant at the present time!

Of course, in addition to reaction with OH radicals, organic compounds can be homogeneously removed from the troposphere by photolysis and reaction with NO_3 radicals and O_3 (and for certain basic amines and hydrazines and other nitrogen-containing heterocycles, by reaction with gas phase HNO_3). While for the majority of organic compounds the reaction with OH radicals is expected to be the major homogeneous tropospheric loss process, these other reactions can dominate over OH radical reaction for certain classes of organics, e.g., photolysis for the alkyl nitrites (Atkinson and Lloyd 1984) and nitrosamines (Tuazon et al. 1984b), reaction with O_3 for the higher alkenes (including the monoterpenes), reaction with the NO_3 radical for the higher alkenes (including the monoterpenes), dimethyl sulfide, furan and pyrrole, and the hydroxy-substituted aromatics (Japar and Niki 1975, Carter et al. 1981, Atkinson et al. 1984e-i, 1985b,c).

As an illustrative example, Table 20 gives calculated atmospheric lifetimes for a series of organics for reaction with OH and NO_3 radicals and with O_3. For these approximate estimates, the room temperature OH radical rate constants, and OH radical, NO_3 radical and O_3 concentrations of 5×10^5 molecule cm^{-3}, 2.4×10^8 molecule cm^{-3} (over continental areas) [Platt et al. 1980, 1981, 1982, 1984] and 7.2×10^{11} molecule cm^{-3} (Singh et al. 1978) have been used.

These estimated, and approximate, lifetimes are consistent with our above discussion, and show that the OH radical reactions are the major tropospheric loss process for the alkanes, haloalkanes, the lower alkenes, the aromatic hydrocarbons and a majority of the oxygen-containing organics.

Table 20. Comparison of Room Temperature Rate Constants and Loss Rates of Selected Organics in the Presence of 7.2×10^{11} molecule cm^{-3} of O_3, 5×10^5 molecule cm^{-3} of OH Radicals, and 2.4×10^8 molecule cm^{-3} of NO_3 Radicals

Organic	OH		O_3		NO_3	
	k^{OH}, cm^3 molecule^{-1} s^{-1}[a]	Loss Rate, day^{-1}	k^{O_3}, cm^3 molecule^{-1} s^{-1}[b]	Loss Rate, day^{-1}	k^{NO_3}, cm^3 molecule^{-1} s^{-1}[c]	Loss rate, day^{-1}
Alkanes and Haloalkanes						
n-Butane	2.5×10^{-12}	0.11	$<10^{-23}$	$<6 \times 10^{-7}$	3.6×10^{-17}	0.0007
1,2-Dibromoethane	2.5×10^{-13}	0.01	$<10^{-23}$	$<6 \times 10^{-7}$	-	-
Alkenes and Haloalkenes						
Ethene	8.5×10^{-12}	0.37	1.8×10^{-18}	0.11	1.1×10^{-16}	0.002
Propene	2.6×10^{-11}	1.1	1.1×10^{-17}	0.7	7.6×10^{-15}	0.16
2-Methyl-2-butene	8.7×10^{-11}	3.8	4.2×10^{-16}	25	9.9×10^{-12}	205
d-Limonene	1.4×10^{-10}	6.0	6×10^{-16}	36	1.4×10^{-11}	130
Trichloroethene	2.4×10^{-12}	0.10	$<3 \times 10^{-20}$	<0.002	-	-
Alkynes						
Acetylene	7.3×10^{-13}	0.03	7.8×10^{-21}	0.0005	-	-
O-, S-, N-Containing						
Acetaldehyde[d]	1.6×10^{-11}	0.7	$\leq 6 \times 10^{-21}$	$\leq$0.0004	2.5×10^{-15}	0.05
Methyl vinyl ketone	1.8×10^{-11}	0.8	4.8×10^{-18}	0.3	-	-

(continued)

Table 20 (continued) - 2

Organic	OH		O_3		NO_3	
	k^{OH}, cm^3 $molecule^{-1}$ s^{-1} [a]	Loss Rate, day^{-1}	k^{O_3}, cm^3 $molecule^{-1}s^{-1}$ [b]	Loss Rate, day^{-1}	k^{NO_3}, cm^3 $molecule^{-1}$ s^{-1} [c]	Loss rate, day^{-1}
Furan	4.0×10^{-11}	1.7	2.4×10^{-18}	0.15	1.4×10^{-12}	29
Dimethyl sulfide	6×10^{-12}	0.26	$<8 \times 10^{-19}$	<0.05	9.7×10^{-13}	20
Thiophene	9.7×10^{-12}	0.4	$<6 \times 10^{-20}$	<0.004	3.2×10^{-14}	0.7
Dimethyl amine[e]	6.5×10^{-11}	2.8	2.6×10^{-18}	0.16	-	-
Hydrazine[e]	6.5×10^{-11}	2.8	$\sim 3 \times 10^{-17}$	~2	-	-
Pyrrole	1.2×10^{-10}	5.2	1.6×10^{-17}	1.0	4.9×10^{-11}	1000
Aromatics						
Toluene	6.2×10^{-12}	0.27	$<1 \times 10^{-20}$	<0.0006	3.6×10^{-17}	0.0007
o-Cresol	4.0×10^{-11}	1.7	2.6×10^{-19}	0.02	2.2×10^{-11}	450

[a] From Atkinson (1985).
[b] From Atkinson and Carter (1984).
[c] From Atkinson et al. (1984e-i, 1985b,c).
[d] Photolysis will also occur, but OH radical reaction will be dominant.
[e] Reaction with gas phase HNO_3 will also occur, and may be the dominant loss process in urban atmospheres.

6. RECOMMENDATIONS FOR FUTURE RESEARCH

The two reviews carried out under this cooperative agreement constitute a large data base for O_3 and OH radical reactions with organics. However, certain areas of uncertainty still remain, especially with regard to the mechanisms of these reactions and the products formed under atmospheric conditions.

While further research is needed to expand the available kinetic data base for the development of a-priori predictive techniques for assessments of atmospheric lifetimes, such research should focus on selected classes of organics. For example, data are needed concerning the O_3 and OH radical reaction rate constants with organics possessing more than one functional group. Such data would allow the reliability of the most recent a-priori predictive technique of Atkinson (1985) to be assessed, and point the way for future experimental and theoretical approaches.

However, at the present time such kinetic data needs are judged to be of relatively lower priority. Instead, the major goal of future research must be to determine the mechanisms and the products formed under atmospheric conditions from the reactions of OH and NO_3 radicals and of O_3 with representatives of the individual classes of organic compounds emitted into the atmosphere. Clearly, such a research effort will require sophisticated analytical instrumentation, large environmental chambers and experienced research staff. However, as noted by Atkinson and Carter (1984) [concerning O_3 reactions] and Atkinson (1985) [concerning OH radical reactions] several research groups have begun to work on this topic. Still greater emphasis on this research area would yield important advances in our understanding of the ultimate environmental impacts of hazardous and toxic chemicals.

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PUBLICATIONS SUPPORTED WHOLLY OR IN PART
BY COOPERATIVE AGREEMENT CR-809247

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